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ON THE POLYCRYSTALLINE FORMS OF GYPSUM AND THEIR OPTICAL BEHAVIOUR

By Sir C. V. Raman and A. K. Ramdas

(*Memoir No.* 48 *from the Raman Research Institute, Bangalore*)

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1. Introduction

Gypsum occurs in nature both as well-developed crystals and as polycrystalline masses. The best known of the massive forms is alabaster; this is a fine-grained white solid. Another naturally occurring variety of gypsum is satin-spar, which is a fibrous material presenting a highly characteristic sheen or lustre from which its name is derived. The present paper is chiefly concerned with a form of gypsum which has come under our notice and which is distinct from either alabaster or satin-spar. It is noteworthy by reason of the very beautiful and interesting optical effects which it exhibits. We have been unable to find any reference to these phenomena in the mineralogical literature, and it would seem that though the material is clearly a distinct species of gypsum, this has not been hitherto recognised and its remarkable optical behaviour has remained unnoticed. We shall proceed to describe the phenomena and explain them in terms of the structure of the material. We have thought it desirable also to include in this paper some observations we have made with alabaster and with satin-spar, and their interpretation in terms of the physical constitution of these varieties of gypsum.

2. Nature of the Material

The species of gypsum which forms the principal subject of this paper presents some external features which enable it to be readily distinguished from the other recognised varieties of gypsum, *viz.*, selenite, satin-spar and alabaster. Like selenite, it may be readily split into slabs or sheets of any desired thickness, but the surfaces thus exposed do not exhibit the smoothness and optical perfection characteristic of the cleavages of selenite. Indeed, they are more appropriately described as planes of parting rather than as cleavages. Another distinctive feature of the material which at once distinguishes it from selenite is that the edges of the blocks or slabs are not smooth but exhibit parallel ridges, suggesting that the material is an aggregate of rod-shaped crystals having a common orientation perpendicular to the planes of parting. Optically, the material does not show the perfect

transparency in all directions characteristic of selenite; neither does it, on the other hand, exhibit the sheen or lustre characteristic of satin-spar. The fact that it readily splits into parallel sheets indicates a certain measure of similarity of its structure to that of the tabular forms of selenite. We infer that the planes of parting are parallel to the crystallographic symmetry plane of gypsum, while the rod-shaped crystals are orientated along the crystallographic symmetry axis. We shall see later that these inferences are supported by the results of a more detailed investigation and we accordingly propose to designate this species of gypsum (which appears to be by no means uncommon) as "fascicular gypsum".

3. THE CIRCLES OF INTERNAL REFLECTION

When a plate of this species of gypsum is held in front of the eye and a distant source of light is viewed *normally* through it, the phenomena illustrated in Fig. 1, Plate XIII are observed. A brilliant circle of light is seen; at the centre of this circle, the source of light appears, but is overlaid by a diffraction pattern consisting of a central disc with concentric surrounding rings. As the plate is tilted away from the normal setting, the outer circle enlarges while the inner diffraction pattern expands and becomes a second circle. This is initially somewhat diffuse by reason of its being a circular diffraction ring with fainter concentric rings on either side (Fig. 2 in Plate XIII). The circle, however, sharpens when the plate is more obliquely set. With a further tilt of the plate, a third circle emerges at the centre of the whole pattern, firstly as a diffraction disc accompanied by rings and later as a well-defined circle of light (Fig. 3 in Plate XIII). As the plate is held more and more obliquely, the angular diameters of all the three circles continue to enlarge, but they remain concentric with each other, and also tend to come closer together (Fig. 4 in Plate XIII). The source itself continues to be visible as a bright point on the second ring in every case. The brightest parts of all the three circles are the regions in the immediate vicinity of this image of the source. However, in a dark room, the complete circles can be seen, and their angular diameters may be increased to any desired extent by giving an appropriate tilt to the plate. At the most oblique settings of the plate, the angular separations of the three circles from each other reach a minimum and then increase once again. Except when they emerge at the centre of the field and display the colours associated with diffraction, the bright circles appear white, thus unmistakably indicating their origin as due to *internal reflection.*

It should be mentioned that the photographs reproduced in Figs. 1 to 4 in Plate XIII, were obtained using a sheet about 1 mm. thick cleaved from a

block of the material. Thin glass plates were fixed on either side with a little canada balsam to eliminate the effect of the optical imperfections of the exterior faces. Essentially the same phenomena are observed with either thicker or thinner sheets. With thick plates, however, the rings become a little broad and the whole field is overlaid by diffuse light; the light source also ceases to be visible on the second ring when the plate is tilted sufficiently. This is not the case with thinner plates; the source of light continues to be visible even at very oblique incidences. The diffraction effects of the kind referred to above are also more conspicuous with the thinner plates.

4. Polarisation of the Internal Reflections

We shall now proceed to describe and illustrate the remarkable features of polarisation exhibited by the circles of internal reflection. These features may be observed by placing a polaroid between the eye and the light source either before or after the plate, and rotating either the polaroid or the plate in its own plane. Strangely enough, the effect of the introduction of the polariser is quite different according as it is set before or after the plate of gypsum. The extent to which the plate is tilted away from the normal is not a matter of importance, since a particular circle of reflection exhibits much the same features of polarisation irrespective of its angular diameter. On the other hand, the orientation of the plate in its own plane with respect to the vibration direction of the polaroid is of the utmost importance. One finds by trial that there are two directions in the plane of the plate perpendicular to each other which we may designate as OX and OZ respectively, with one or the other of which the vibration direction of the polaroid should coincide to produce the maximum effects. If the vibration direction of the polaroid bisects the angle between OX and OZ, the polarisation effects are not observed.

Figures 5, 6, 7 and 8 in Plate XIV illustrate the changes in the relative intensities of the three circles of reflection resulting from the insertion of a polaroid. (The plate of gypsum was set obliquely, and the camera recorded only the more intense parts of the circles.) The legends entered below each figure indicate the location of the polaroid and its setting. P indicates that the light was polarised before entering the plate of gypsum, while A indicates that light was unpolarised at entry but passed through a polaroid after reflection. On a comparison of Figs. 5 and 6 it will be seen that a transfer of the polaroid from the front to the back of the plate results in reversing the behaviour of the first and the third circles of reflection, leaving the second or middle circle unaffected. A comparison of Fig. 7 with Fig. 8 shows a similar change in the opposite direction, while a comparison of Fig. 5 with Fig. 7 or of Fig. 6 with Fig. 8 exhibits the effect of setting of the vibration direction of the polaroid along OZ instead of along OX.

The significance of the facts stated above is clear, namely, that in the internal reflections which give rise to the first and third circles, the vibration direction changes from OX to OZ or *vice versa* in the act of reflection; the former change gives us the first circle of reflection, while the third circle of reflection is associated with a change of the vibration direction from OZ to OX. On the other hand, in the middle or second circle of reflection, there is no change of the vibration direction, OX remaining as OX and OZ as OZ.

If both a polariser and an analyser are used, their effects are combined, as will be seen from Fig. 9 to Fig. 12 reproduced in Plate XIV; the legends below each figure give the settings of both the polariser and analyser. It will be noticed that when they are crossed, the second or middle circle is greatly weakened, while the first appears with maximum intensity and the third circle is totally extinguished or *vice versa*. On the other hand, when the polariser and the analyser are set parallel, both the first and the third circle appear greatly weakened, while the second or middle circle appears with maximum intensity.

It may be remarked that the photographs reproduced as Figs. 5 to 12 in Plate XIV, were recorded with a specimen which exhibited the polarisation effects most conspicuously. Other specimens indeed show similar effects but not always in such a striking manner. The degree of perfection of polarisation was also found to vary over the area of the specimens.

5. ORIGIN OF THE REFLECTIONS

It is evident that the phenomena described above are all interconnected and that an explanation of the same has to be sought for on the basis of the geometric and optical characters of the polycrystalline aggregate. Earlier in the paper, we have suggested that the material consists of rod-shaped crystals having a common orientation for their crystallographic symmetry axis. The latter is an axis of the optic ellipsoid of gypsum. Had the two other optic vibration directions also been the same for all the rods, the material would be optically homogeneous and indistinguishable from selenite. Hence we are compelled to assume that the two other optic vibration directions in the plane perpendicular to the rods are not identical for all of them.

Holding a plate of the material between crossed polaroids and viewing an extended source of light through it, we find on rotating the plate in its own plane, two mutually perpendicular settings in which there is a maximum restoration of light and two others intermediate between them in which there is nearly but not quite complete extinction of light. A *small* bright source of light viewed through the combination at the latter settings is, however, extinguished more or less perfectly.

The situation indicated above may be summed up by the statement that the plate considered as a whole has two mutually perpendicular directions as its optic vibration directions, though the individual rods in the aggregate may deviate therefrom to a greater or less extent. That this is the actual situation is indicated by the appearance of the plate under a microscope when viewed between crossed polaroids. Rotating the plate in its own plane, two settings are found in which there is a minimum of light in the field but by no means complete extinction everywhere. The greater part of the plate appears dark, but there are areas in which there is a notable restoration of light. At these two settings, the directions in the plate designated as OX and OZ in the description of the polarisation effects are also the vibration directions of the polariser and the analyser. It is noticed further that the regions on the plate which give the most marked extinctions are those which give the most perfect polarisation of the circles of reflection, while the areas in which the extinctions are imperfect, also show marked imperfection of the polarisation of the circles of reflection.

6. The Geometric Character of the Reflections

It is a familiar result in geometrical optics that when a pencil of light is incident on a cylindrical rod in a direction making an angle θ with its generators, the rays reflected by its surface lie along the generators of a right circular cone whose semi-vertical angle is also θ and which has its axis parallel to the length of the cylinder. In the present case, however, the reflections occur at intercrystalline boundaries within a birefringent solid, and hence the angles of incidence and of reflection of the light at these boundaries are not necessarily equal. Actually, as a result of the birefringence of the material, an incident pencil of light would divide on entry into the plate into two pencils polarised differently which travel in different directions with different velocities. A further subdivision would occur in the act of reflection at the boundaries, giving us four reflected pencils in all. However, owing to the special circumstance that the external surfaces of the plate are normal to an axis of its optic ellipsoid, two of these pencils would obey the ordinary laws of reflection and would emerge from the plate in identical directions, though their planes of polarisation are mutually perpendicular. For the two other pencils, the angle of reflection would be greater or less than the angle of incidence as a consequence of the planes of polarisation and therefore also the wave-velocities being different for the incident and reflected pencils. Thus, in the final result, we would have, instead of a single cone of reflected rays, three such cones exhibiting the polarisation effects already described; the central or the middle one would have the direction of the light source as one of its generators, and hence the source would appear as a luminous point on that circle.

The correctness of the explanations set forth above is confirmed by a few simple calculations and observations. The angles of incidence and of reflection of light inside a birefringent medium are connected by the relation $\mu_i \cos \theta_i = \mu_r \cos \theta_r$, where θ_i and θ_r are the glancing angles which incident and reflected rays make with the reflecting boundary, and μ_i and μ_r are the corresponding refractive indices. In our present problem, the two refractive indices under consideration are 1·521 and 1·530. For normal incidence on the surface of the plate, $\theta_i = 0$, while the values of θ_r comes out respectively as 6° 18′, 0°, and imaginary for the three circles of reflection. Accordingly, the angles of emergence for the first and second circles come out as 9° 39′ and 0° respectively while the third circle is non-existent, in close agreement with the observations. For the case in which the third circle is just visible, the angular radii of the first, second and third circles on emergence come out as 13° 42′, 9° 39′ and 0° respectively, once again in close agreement with the results of observation.

The reflections at the intercrystalline boundaries arise from the fact that the optical polarisabilities of the material on either side of such a boundary differ in magnitude or direction or both. The birefringence of gypsum being very weak, such differences would necessarily be small. The strong reflections actually observed are a consequence of the incidence of the light being very oblique in the cases under study. This is clear from the fact that the circles of reflection display their maximum intensity in the regions not too remote from the image of the light source appearing located on the second circle (see Figs. 2, 3 and 4, Plate XIII). The variation of intensity exhibited by the first circle of reflection over its circumference (Fig. 1 in the same plate) has a different origin : it exhibits the fact that the reflecting power is a function of the azimuth of incidence of the light on the boundary, besides being dependent on the angle of incidence which in this case has the maximum value of 90°.

A few brief remarks must suffice in explanation of other features which are observed and which have been referred to earlier. The diffraction phenomena associated with the circles of internal reflection are evidently a consequence of the limitation of the effective aperture due to the oblique incidence of light on the reflecting surfaces. They naturally become most conspicuous when such incidence is nearly grazing. Phenomena closely resembling them may be observed when light from a distant source is reflected obliquely at the surface of a short cylinder of glass.

The reflections of light at the intercrystalline boundaries in the material would necessarily result in a progressive extinction of the incident light beam

in traversing the material. The greater the thickness of the plate and the more it is tilted away from the normal, the larger would be the number of reflecting surfaces traversed by the incident light, and hence also the more rapid would be its extinction, as is actually observed.

The diffuse radiation which appears overlying the circles of reflection, especially with thick plates, and the broadening of the circles of reflection which is noticed with such plates when they are held obliquely may be the result of a lack of perfect parallelism in the orientation of the rod-like crystals within the material. Another factor which would also result in a diffusion of light is the *refraction* of the light beams in their passage through the successive intercrystalline boundaries. That such refraction does play an important role is suggested by the partial polarisation of the second circle of reflection which is noticed when the plate is tilted considerably away from the normal.

7. Optical Behaviour of Transverse Sections

In the foregoing, it has been assumed that the rod-like crystals of which the material is composed are parallel to each other and to the crystallographic symmetry axis. If this were strictly the case, a plate of the material so cut that its faces are parallel to the rods should exhibit the following optical behaviour: (1) a light beam polarised with its electric vector parallel to the rods should be freely transmitted by the plate without diffusion or extinction; (2) on the other hand, if the electric vector is perpendicular to the rods, the optical heterogeneity of the material should exhibit itself and result in a strong diffusion and extinction of the light in its passage through the plate, the diffused radiation appearing as a fan of rays in a plane transverse to the rods.

These indications of theory can be tested by observation and are found to be in general accord with the facts but not completely so. A distant source of light viewed through such a plate held normally continues to be visible in focus. Further, it is also completely polarised with its electric vector parallel to the length of rods. However, one also observes a fan of diffracted rays accompanying the transmitted light spread out in a plane transverse to the rods, and this exhibits a partial polarisation in the same sense as the transmitted light. A tilt of the plate away from its normal setting results in extinguishing the transmitted light, if such tilt is in a plane parallel to the rods. On the other hand, a tilt in the perpendicular plane has no such effect.

From the foregoing observations one infers that the structure of the material is approximately but not quite accurately that assumed. This also becomes evident when a plate cut in the same fashion is examined between

crossed polaroids under a microscope. A complete extinction is not obtained in any setting of the plate. There is, however, a notable diminution of intensity of the light seen in the field, when the direction of the rods coincides with the vibration direction of either the polariser or the analyser.

8. SOME OBSERVATIONS WITH ALABASTER

Alabaster is opaque to light, evidently as a consequence of the birefringence of gypsum, though light can penetrate by diffusion through very considerable thicknesses. The extent of such penetration is highly variable and such variations appear to be connected with the structure of the material including especially the size of the crystallites of which it is composed.

It appeared to be of interest to investigate whether a transmission of light in the true optical sense could be observed with alabaster if it be thinned down sufficiently. With coarse-grained varieties the test does not succeed, since we soon arrive at a stage at which the thickness of the test plate is comparable with the size of the individual crystallites which can then be observed to transmit light independently of each other. Fine-grained varieties of alabaster, however, can be thinned down sufficiently to enable a true optical image of a distant and brilliant source of light to be seen through the plate. The image appears overlaid by a diffuse halo, the structure and angular extension of which are determined by the thickness of the plate and the grain size of the substance. The optical transmission is readily distinguished from the overlying halo by its brilliance and its perfect sharpness. It is completely extinguished when the plate is held between crossed polaroids, whereas the halo continues to be visible in the same circumstances though with diminished intensity.

9. THE STRUCTURE AND OPTICAL BEHAVIOUR OF SATIN-SPAR

The fibrous nature of satin-spar is conspicuously evident from its very appearance. A beam of light is spread out by reflection at the surface into a fan of light in a plane transverse to the length of the fibres. A plate of the material having its faces parallel to the fibres differs very strikingly in its behaviour from that described in Section 7 above. A distant source of light is invisible when viewed through it, all that is observed being a fan of diffracted rays transverse to the fibres and this is found to be completely unpolarised. This behaviour is readily explicable as a consequence of the birefringence of gypsum and the known crystallographic orientation of the fibres.

As is to be expected, light is found to penetrate along the fibres rather more freely than in the transverse direction. A distant bright source of light can indeed be seen if viewed through a rod of the material exactly along

FIG. 1

FIG. 2

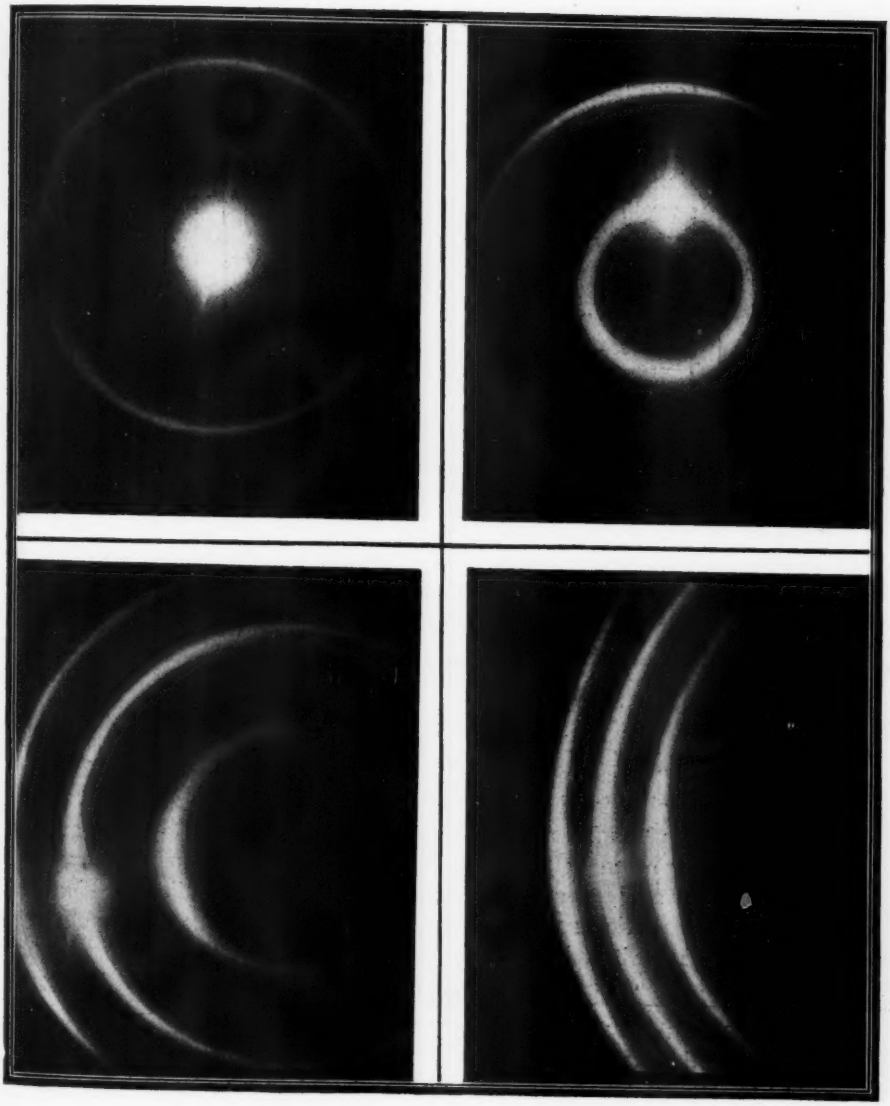
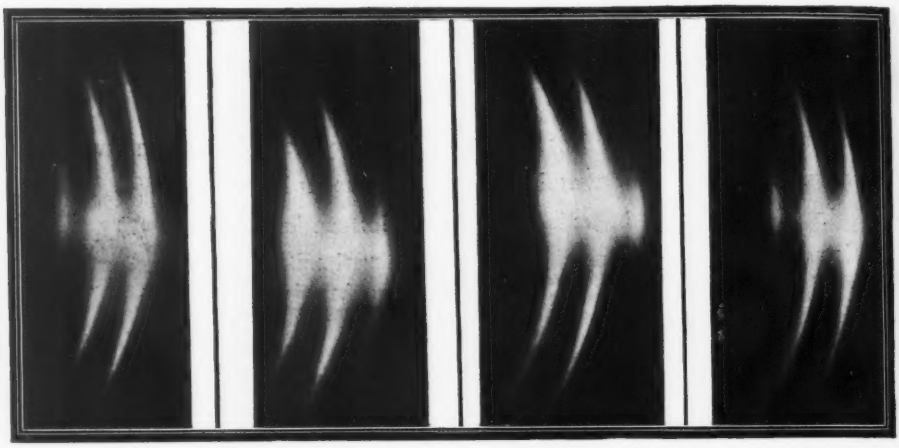


FIG. 3

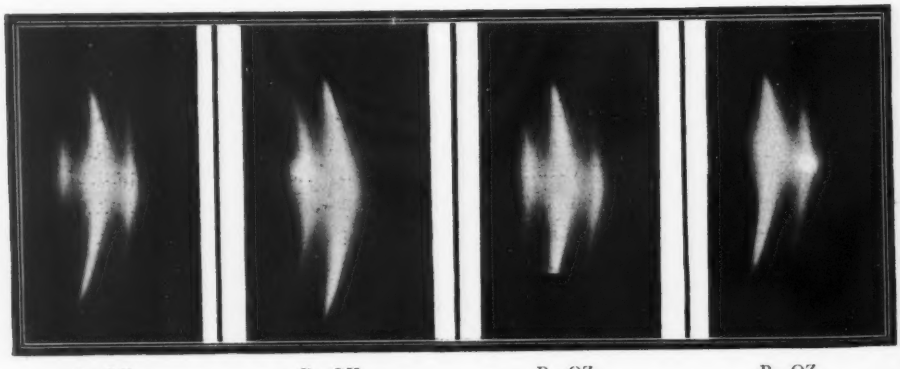
FIG. 4

FIG. 5 FIG. 6 FIG. 7 FIG. 8



P—OX A—OX P—OZ A—OZ

FIG. 9 FIG. 10 FIG. 11 FIG. 12



P—OX
A—OX

P—OX
A—OZ

P—OZ
A—OZ

P—OZ
A—OX

its fibres, but appears spread out into a diffuse patch of light. If the rod be tilted a little, this transforms into a diffuse circle of light with a darker area within, the diameter of which increases with the tilt. The brilliancy and sharpness of the phenomena observed with fascicular gypsum are conspicuously absent in the present case, neither are any polarisation effects observed.

10. Summary

The paper brings to notice the remarkable optical effects exhibited by a polycrystalline form of gypsum which is different from both alabaster and satin-spar in its structure. It is not a fibrous material but consists of fine rods orientated nearly parallel to the *b*-axis of gypsum and exhibits a ready cleavage along planes perpendicular to that axis. A source of light viewed through a plate of the material exhibits, in general, three concentric circles which are polarised in a characteristic fashion. The source itself appears as a luminous point on the second or middle circle. It is shown that these circles arise by reason of the reflection of light at the boundaries between the rod-like crystals composing the material, for which the name "fascicular gypsum" is accordingly proposed. A theoretical explanation of the phenomena is given and photographs of the same are reproduced. Observations on the optical behaviour of alabaster and of satin-spar are also reported.

ON RELATIVISTIC PARTICLES IN HIGH ENERGY SHOWERS

By Rama

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Received February 22, 1954

(Communicated by Prof. B. Peters, F.A.SC.)

SEVENTY-NINE high energy showers have been investigated for determining:

(1) the interaction cross-section for shower particles in emulsion.

(2) the ratio[1] of neutral π-mesons to charged shower particles.

For these investigations, a nuclear emulsion block detector[2] consisting of 24 Ilford G-5 stripped emulsions 600 μ thick, and $4'' \times 6''$ lateral dimensions, was used. After processing the emulsions were so aligned that the tracks of all charged particles which entered or originated in the stack during a balloon flight could be followed from emulsion to emulsion.

The showers used by us were produced by primaries with energies lying between 50 and 1,000 Bev. per nucleon and the number of charged shower particles in each shower varied between 5 and 40 per incident nucleon. Six such showers produced by heavy primaries were located by following the tracks of heavy primaries from the outside plates into the stack. The remaining showers were found by normal scanning. The energy of the primary was in each case estimated from the opening angle of the shower, using the relation $E/MC^2 = 2/\theta_{\frac{1}{2}}^2$, where $\theta_{\frac{1}{2}}$ is the half angle of the cone containing half the number of shower particles around the shower axis.

In all, 1,635 shower particles were examined for a total track length of 439 cm. in emulsion and 15 secondary interactions were observed corresponding to an interaction mean free path of $29{\cdot}3 \pm 7{\cdot}6$ cm. The term 'secondary interaction' as used here denotes not only stars but charge exchange scattering (no case was observed) as well as ordinary scattering provided the scattering angle exceeds 10° (one case was observed).

The data on secondary interactions in similar investigations reported previously from this laboratory and Bristol is given in Table I.

Combining all the results, we get an interaction mean free path of $28{\cdot}4 \pm 4{\cdot}8$ cm. for shower particles in emulsion, while the value of interaction mean free-path corresponding to geometrical interaction cross-section in G-5 emulsion is 27 cm. (This value is based on a nuclear radius of

TABLE I

Primary energy region	Track length (cm.)	No. of interactions	Authors
8,000 Bev.	301	8	Lal *et al.* [3]
50–3,000 Bev.	129	5	Daniel *et al.* [4]
20,000 Bev.	140	4	Mulvey[5]
50–1,000 Bev.	439	15	Present work
Total ..	909	32	

$1{\cdot}38\times10^{-13}\,A^{\frac{1}{3}}$ cms. for each constitutent nucleus of atomic weight A.) The result indicates that probably all shower particles interact with nearly geometric cross-section. However, witin statistical accuracy the result allows still a small admixture (less than 19%) of non-interacting shower particles.

It has been observed that in the secondary stars produced by shower particles the number of heavy prongs, n_h, is generally very small. The distribution of secondary stars with respect to n_h is given in Table II.

TABLE II

n_h ..	0	1	2	3	4	5	6	7	8	9	10	11	12	13
No. of secondary stars	1	8	..	1	..	..	2	..	..	1	1	..	1	..

The number of charged shower particles, n_s, in these interactions varies from 0 to 4. In the secondary interactions with n_s varying from 1 to 4, we find the average n_h to be < 4. In stars having similar number of charged shower particles but produced by all cosmic ray components (presumably mostly nucleons), Camerini *et al.*,[6] find the average n_h to be about 10. In both cases the energies of the particles responsible for the interaction lie in about the same energy interval. There is then some indication that meson production by particles emerging from energetic showers causes less excitation in the target nucleus than meson production by nucleon. A similar indication was obtained earlier.[3]

The ratio[1] of neutral pions to charged shower particles has been determined by counting electron pairs associated with showers upto a maximum distance of 6 mm. (·16 conversion units) from the shower origin. From the results it appears that cascade multiplication should be less than 20%

upto ·16 conversion units, and negligible at ·12 conversion units. We obtain the ratio of neutral pions to charged shower particles as ·40 ± ·08. Combining this result with other similar investigations,[1] the ratio becomes ·40 ± ·04.

If one assumes:

(1) that all pairs observed derive from neutral π°-meson;

(2) that the ratio of neutral to charged π-meson production is $\frac{1}{2}$; and

(3) that the charged shower particles contain not more than 10% protons,

one concludes that the number of shower particles which are neither π-mesons nor protons should be less than 18%.

We observed only two deflections of $\sim 5^\circ$ each in all the 1,635 shower tracks. These two particular tracks before the deflection could be identified as due to π-mesons. One case could be interpreted as due to π-μ decay or due to scattering; the second case as that of scattering only.

We observed no event which could be interpreted as the decay of K-meson into L-meson.

Two events were observed in which the shower particle gives rise to only one grey proton track. If they are assumed to be the decays of charged hyperons into proton and a neutral pion, the Q-values turn out very large (·4 and 1·4 Bev. respectively). It seems very unlikely that either of these events is caused by hyperon decay.

I am extremely indebted to Professor B. Peters for his guidance and keen interest throughout this work. I am also thankful to Dr. R. R. Daniel, Mr. G. B. Friedmann, Miss P. A. Irani, Mr. D. Lal and Mr. Y. Pal for their co-operation.

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SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XLII. A New Synthesis of 5 : 6 : 7-Trihydroxy Isoflavone Derivatives

By V. B. Mahesh, N. Narasimhachari and T. R. Seshadri, F.A.Sc.
(From the Department of Chemistry, Delhi University)

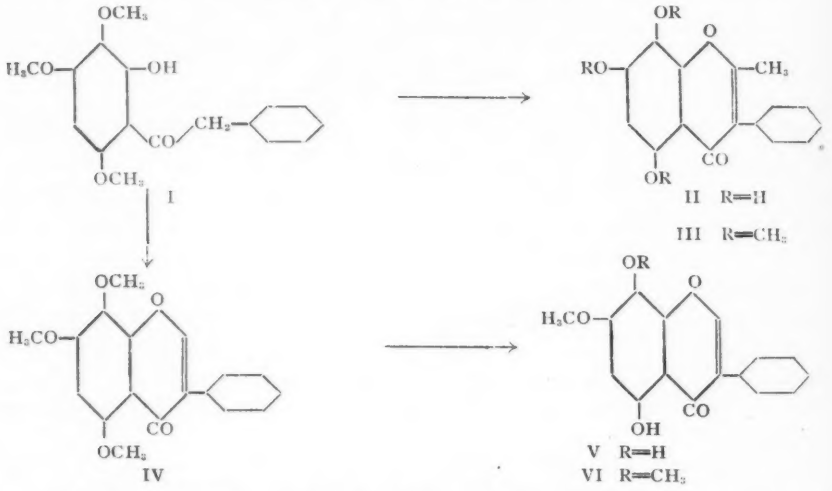
Received October 15, 1953

In an earlier paper[1] a convenient method of preparing 5 : 6 : 7-trihydroxy isoflavones starting from antiarol was described. Meanwhile experiments had been in progress in this laboratory to find out alternative methods for their synthesis. The methods known to be successful in the case of flavones were first examined. As already pointed out the nuclear oxidation of 2-hydroxy-4 : 6-dimethoxy-phenyl benzyl ketone did not proceed satisfactorily.[2] This may partly be attributed to the very low solubility of the ketone in alkali but even the addition of pyridine did not give a satisfactory yield. The second convenient method of preparation is the conversion of the more readily available 5 : 7 : 8-trihydroxy (methoxy) compounds into the corresponding 5 : 6 : 7-trihydroxy compounds by means of boiling hydriodic acid. This has been very successful in the case of flavones and has been used by Rao, Seshadri and Viswanadham[3] as preparative method; but this isomeric change does not take place under the same conditions in the case of flavonols and isoflavones[2] and therefore is not available for the present purpose.

A new route for the conversion of 5 : 7 : 8-trihydroxy (methoxy) isoflavones into the corresponding 5 : 6 : 7-trihydroxy (methoxy) compounds has now been examined. Earlier tectorigenin dimethyl ether was prepared by Shriner and Stephenson[4] by using 2 : 6-dihydroxy-3 : 4 : 4′-trimethoxy-phenyl-benzyl ketone as the intermediate. The synthesis of the intermediate was rather tedious and involved a number of difficult steps. Attempts have now been made to prepare this type of ketone in a different way starting from the easily available 5 : 7 : 8-trihydroxy (methoxy) isoflavones by alkali fission. Thus this constitutes essentially a method of conversion of one isoflavone into its isomer.

2-Methyl-5 : 7 : 8-trihydroxy isoflavone (II) was originally made by the nuclear oxidation of 2-methyl 5 : 7-dihydroxy isoflavone.[2] It could be subjected to partial methylation to yield the 7 : 8-dimethyl ether (XVI). Owing

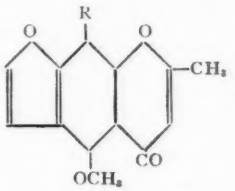
to poor yields in the nuclear oxidation the method is not convenient. In the second method 1:2:3:5-tetramethoxy benzene is condensed with phenyl-acetyl chloride to yield 2-hydroxy-3:4:6-trimethoxy-phenyl-benzyl ketone (I). On vigorous acetylation the 2-methyl isoflavone (III) is obtained. Here also the yields are comparatively poor and the methoxy isoflavone being low melting does not easily crystallise. The 5:7:8-trimethoxy isoflavone (IV) has also been obtained directly from the ketone (I) by the action of sodium and ethyl formate. The overall yields are better in this case and hence it has been prepared in larger quantities for detailed study.



To obtain 5-hydroxy-7:8-dimethoxy isoflavone (VI) from the 5:7:8-trimethoxy compound (IV) two methods could be used. In the first one the trimethoxy isoflavone (IV) is subjected to controlled demethylation with hydriodic acid when it yields 7-methoxy-5:8-dihydroxy isoflavone[5] (V) and by partial methylation the required dimethyl ether (VI) is obtained. It may be mentioned that the use of hydriodic acid under controlled conditions has been studied in great detail and a number of 7-methyl ethers of isoflavones prepared.[6]

The same compound (VI) could be prepared by a simpler method which is based on the observation that concentrated hydrochloric acid brings about easy demethylation of the 5-methoxy group alone yielding the product in an almost quantitative yield. The reagent has been used earlier for the demethylation of the 5-methoxy group in visnagin[7] (VII) and kellin[8] (VIII) and it does not cause isomeric change. In the field of isoflavones the reagent

was first used by Dhar, Narasimhachari and Seshadri.[9] This method is definitely better and simpler than the two stage process described earlier and yields are very good.

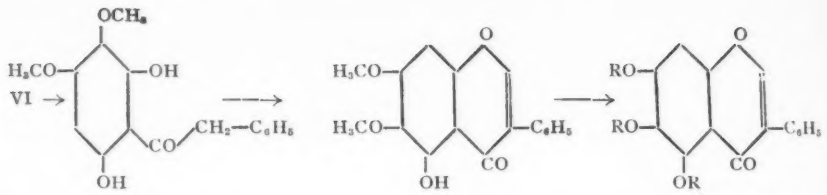


VII R=H
VIII R=OCH_3

The isoflavone (VI) is then subjected to fission with hot 8% absolute alcoholic potash. The resulting 2: 6-dihydroxy-3: 4-dimethoxy-phenyl-benzyl ketone (IX) is best purified by dissolving in aqueous sodium carbonate and reprecipitating with acid. When it is condensed with ethyl formate and sodium at 0° the resulting compound gives all the reactions characteristic of 5-hydroxy isoflavone derivatives. But it is different from 5-hydroxy-7: 8-dimethoxy isoflavone (VI) in melting point and colour reactions and therefore should be 5-hydroxy-6: 7-dimethoxy isoflavone (X). On complete demethylation with hydriodic acid or anhydrous aluminium chloride in benzene solution it gives a trihydroxy compound [5: 6: 7-trihydroxy isoflavone (XI)], which does not differ markedly from its 5: 7: 8-isomer in reactions. But the mixed melting point shows marked depression and the derivatives differ markedly.

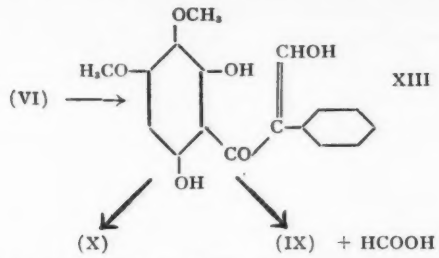
The differences are brought out clearly in the following table:—

S. No.	Compound	5 : 7 : 8–substituted isoflavone derivative	5 : 6 : 7–substituted isoflavone derivative
1	Trihydroxy compound— (*a*) melting point (*b*) colour with ferric chloride	 280–282° green changing to brown	 282–283° (decomp.) olive green changing to deep brown
2	Triacetyl derivative (melting point)	 206–208°	 185–186°
3	Trimethyl derivative (melting point)	 150–151°	 165–166°
4	5–Hydroxy dimethyl ether (*a*) melting point (*b*) colour with ferric chloride	 159–160° green	 203–205° bluish violet
5	5–Acetoxy-dimethyl ether (melting point)	 143–144°	 121–123°

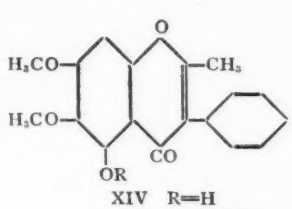


An interesting observation has been made in the course of the fission of 5-hydroxy-7: 8-dimethoxy isoflavone (VI), which indicated the presence of a compound sparingly soluble in aqueous alkali. It was actually this observation that led to the purification of 2: 6-dihydroxy-3: 4-dimethoxy-phenyl-benzyl ketone (IX) with aqueous sodium carbonate. The carbonate insoluble compound melted at 203–05°, gave a bluish violet colour with ferric chloride, was very sparingly soluble in aqueous alkali and was identical with 5-hydroxy-6: 7-dimethoxy isoflavone (X); a mixed melting point with an authentic sample of this structure described earlier showed no depression. A possible explanation for this peculiar and novel result suggests itself from the recent work of Rajagopalan, Narasimhachari and Seshadri[10] on the use of methyl formate in the isoflavone condensation. They suggested that the ω-formyl or hydroxymethylene (see XIII) derivative of a phenyl-benzyl ketone which may be the initial product of the condensation, may undergo change in two directions; one involving simple isomeric change leads to a 2-hydroxy isoflavanone while the other involving a dehydration leads to the isoflavone (X) itself. They considered that on the alkalinity of the medium would depend the course of the reaction; a higher alkalinity favours dehydration, while in the absence of it isomeric ring closure takes place.

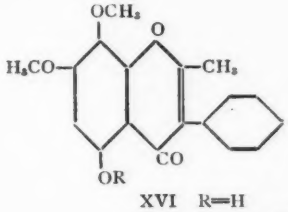
In the present case the alkali hydrolysis of the isoflavone (VI) leads to the opening of the pyrone ring, forming a hydroxymethylene compound (XIII) which then undergoes further fission yielding the phenyl-benzyl ketone (IX) and formic acid. A small portion of (XIII) seems to undergo ring closure instead of fission and as in several similar cases the ring closure from this open structure involves the hydroxyl which is para to a methoxyl thus giving rise to the isoflavone (X). This, therefore, constitutes a direct isomeric change of the 5: 7: 8-hydroxy (methoxy) type to the 5: 6: 7-hydroxy (methoxy) type in isoflavones under alkaline conditions. The yield of the isomeric compound is however low and the reaction is not therefore of preparative value. But the change effected in two stages, the ketone forming the intermediate stage is definitely useful.



With acetic anhydride and sodium acetate the 2: 6-dihydroxy-3: 4-dimethoxy-phenyl-benzyl ketone (IX) undergoes isoflavone ring closure to yield 2-methyl-5-acetoxy-6: 7-dimethoxy isoflavone (XV) which on deacetylation gave 2-methyl-5-hydroxy-6: 7-dimethoxy isoflavone (XIV). This and its acetate are different from 2-methyl-5-hydroxy-7: 8-dimethoxy isoflavone (XVI) and its acetate (XVII). Its identity is confirmed by a comparison with a sample of 2-methyl-5-hydroxy-6: 7-dimethoxy isoflavone prepared by the partial demethylation of 2-methyl-5: 6: 7-trimethoxy isoflavone described by Krishnamurty and Seshadri.[1]



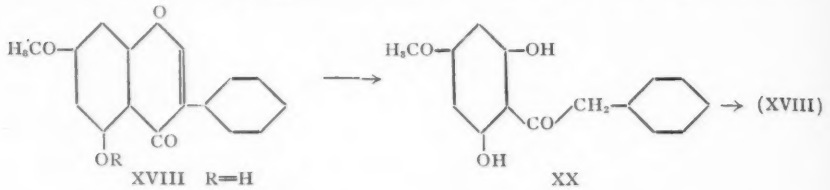
XIV R=H
XV R=CH_3CO



XVI R=H
XVII R=CH_3CO

As an exploratory study during the earlier stages of this work two points had to be considered. Firstly not much work was known on the controlled fission of hydroxy isoflavones to yield the corresponding phenyl-benzyl ketones. Hence it was necessary to study the simplest example in order to get a preliminary idea of the course of the reaction, the nature of the products and their yields. The easily available 5-hydroxy-7-methoxy isoflavone (XVIII) was chosen for this study and it was prepared from 5: 7-dimethoxy isoflavone (XIX) by demethylation using hydriodic acid at 110° and also boiling concentrated hydrochloric acid. On fission with 8% absolute alcoholic potassium hydroxide and purifying the fission product using aqueous sodium carbonate 2: 6-dihydroxy-4-methoxy-phenyl-benzyl ketone (XX) was obtained. The analytical values and the reactions of the ketone agreed with its expected structure. Its constitution was further confirmed by reconversion into the original 5-hydroxy-7-methoxy-isoflavone (XVIII).

Secondly, the use of polyhydroxy ketones for isoflavone condensations using the ethyl formate method has not been commonly adopted. The dihydroxy ketone (XX) gives a satisfactory yield of 5-hydroxy-7-methoxy isoflavone indicating that 2: 6-dihydroxy ketones are in general suitable for this condensation. This is further supported by the more complex example given earlier.



After the work described in this paper was completed we read the communication of Baker *et al.*[11] in which they reported the isomerisation of 5: 7: 8-trihydroxy isoflavones when boiled for eight hours with hydrobromic and acetic acids. In their earlier work Narasimhachari, Row and Seshadri[2] reported the absence of isomeric change when 5: 7: 8-trimethoxy isoflavones were demethylated with hydriodic acid and supported their conclusion by remethylation to the original isoflavone trimethyl ethers. They did not however possess authentic samples of 5: 6 : 7-trihydroxy derivatives for comparison. As the result of the present work these have become available and the earlier observations of Narasimhachari, Row and Seshadri,[2] are found to be correct. Baker *et al.*[11] however report that the conditions of the reaction are the deciding factor, whether or not rearrangement occurs and the details are not yet fully available.

In the same communication Baker *et al.*, report differences in the ring closure using different reagents. Ethyl formate is reported to give the 5: 6: 7-isomer from 2: 6-dihydroxy-4: 5: 4′-trimethoxy-phenyl-benzyl ketone whereas ethyl oxalyl chloride yields the 5: 7: 8-isomer from 2: 4: 6: 4′-tetrahydroxy-5-methoxy ketone. The results recorded in the present paper confirm their observation regarding the ethyl formate condensation.

EXPERIMENTAL

2: 6-*Dihydroxy-4-methoxy-phenyl-benzyl ketone* (*XX*)

5-Hydroxy-7-methoxy isoflavone (XVIII) required for this preparation was made from 5: 7-dimethoxy isoflavone (XIX) as follows: To 5: 7-dimethoxy isoflavone (1 g.) was added concentrated hydrochloric acid (15 c.c.) and mixture boiled under reflux; the isoflavone quickly dissolved yielding a yellow solution and a sticky semi-solid separated in the course of half an

hour. The mixture was then diluted with water (50 c.c.) and cooled well. The aqueous solution was decanted off and the sticky solid treated with a little alcohol (5 c.c.) when it turned rapidly into a crisp solid. It crystallised from ethyl acetate as stout rectangular prisms melting 140–41°. Yield 0·9 g. A mixed melting point with an authentic sample prepared by the method of Aghoramurthy *et al.*[6] was undepressed.

5-Hydroxy-7-methoxy isoflavone (1 g.) was dissolved in 8% absolute alcoholic potassium hydroxide (15 c.c.) and the solution refluxed for four hours. As much alcohol as possible was then removed under reduced pressure by heating on a boiling water-bath. The residue was dissolved in water and the solution acidified with hydrochloric acid. The product was directly taken in ether and the ether solution extracted thrice with 10 c.c. portions of 5% aqueous sodium carbonate. On acidifying the combined carbonate extract the ketone was obtained which crystallised as pale brown prisms from dilute methanol and melted at 142–43°. It gave a violet colour with ferric chloride. Yield 0·3 g. (Found: C, 69·2; H, 5·7. $C_{15}H_{14}O_4$ requires C, 69·7; H, 5·4%).

Conversion into 5-hydroxy-7-methoxy isoflavone (XVIII)

The above ketone (0·6 g.) was dissolved in ethyl formate (5 c.c.) and cooled in ice. Powdered sodium (0·5 g.) cooled in ice, was added to the above solution in small quantities at a time. The mixture was allowed to stand in a refrigerator for 48 hours. Ice pieces were added to it and the excess of ethyl formate was removed under reduced pressure. On cooling the oily liquid initially formed soon solidified. It crystallised from ethyl acetate as stout rectangular prisms melting at 140–41°. Yield 0·3 g. The colour reactions agreed with those of the authentic sample of 5-hydroxy-7-methoxy isoflavone and the mixed melting point was undepressed.

5-Hydroxy-7 : 8-dimethoxy isoflavone (VI)

This was first made by following the method of Narasimhachari, Row and Seshadri[2] employing partial methylation of 5 : 7 : 8-trihydroxy isoflavone.

It has now been obtained by the partial demethylation of 5 : 7 : 8-trimethoxy isoflavone (1 g.) just in the same way as with 5 : 7-dimethoxy isoflavone using concentrated hydrochloric acid as demethylating agent. It crystallised from alcohol as aggregates of stout rhombic prisms melting at 159–60°. Yield 0·8 g. It was identical with the product described earlier.[2] 5-Acetoxy-7 : 8-dimethoxy isoflavone obtained by heating the 5-hydroxy derivative with acetic anhydride and pyridine crystallised from ethyl acetate as colourless long rectangular rods and prisms melting at 143–44°. (Found: C, 66·5; H, 4·5. $C_{19}H_{16}O_6$ requires C, 67·0; H, 4·7%.)

2-*Methyl*-5-*hydroxy*-7 : 8-*dimethoxy isoflavone* (*XVI*)

(*a*) *Partial methylation.*—2-Methyl-5 : 7 : 8-trihydroxy isoflavone[2] (II) (0·6 g.) was refluxed in dry acetone (70 c.c.) with dimethyl sulphate (0·45 c.c.) and anhydrous potassium carbonate (2 g.) for six hours. The potassium salts were filtered off and washed with hot acetone. On distilling off acetone from the filtrate a yellow sticky solid was obtained. It did not solidify even on long keeping. It was therefore converted into its acetate by refluxing with acetic anhydride and pyridine and then pouring on ice. The solid crystallised from alcohol as colourless narrow rectangular plates melting at 207–208°. (Found: C, 66·4; H, 4·8. $C_{20}H_{18}O_6 \cdot \frac{1}{2}H_2O$ requires C, 66·1; H, 5·2%.) The acetate was deacetylated by heating it with alcoholic hydrochloric acid (1 : 1; 5 c.c.) for 10 minutes. On diluting with water a sticky mass separated, the mother liquor was decanted off and the residue dissolved in methyl alcohol (2 c.c.). On allowing it to stand for a number of days in the refrigerator pale yellow tiny prisms having a melting point of 168–69° separated. (Found: C, 69·7; H, 5·1. $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%).

(*b*) *Partial demethylation.*—2-Methyl-5 : 7 : 8-trimethoxy isoflavone required for this experiment was obtained by heating 2-hydroxy-3 : 4 : 6-trimethoxyphenyl-benzyl ketone (6·8 g.) with fused sodium acetate (10 g.) and acetic anhydride (40 c.c.) at 170–80° for sixteen hours. After treatment with ice the solid product crystallised from alcohol as transparent stout rectangular prismatic rods melting at 93–94°[2]. Yield 1·8 g.

Starting with 2-methyl-5 : 7 : 8-trimethoxy isoflavone (0·8 g.) the partial demethylation was carried out just in the same way as with 5 : 7-dimethoxy isoflavone using concentrated hydrochloric acid as demethylating agent. Due to difficulty in crystallisation the crude product was directly converted into the acetate which on crystallisation from alcohol separated as colourless narrow rectangular plates melting at 207–08°. Mixed melting point with the above sample of 5-acetoxy-7 : 8-dimethoxy-2-methyl isoflavone was undepressed.

2 : 6-*Dihydroxy*-3 : 4-*dimethoxy-phenyl-benzyl ketone* (*IX*)

(*a*) *By the fission of* 5-*hydroxy*-7 : 8-*dimethoxy isoflavone* (*VI*).—5-Hydroxy-7 : 8-dimethoxy isoflavone (0·8 g.) was dissolved in 8% absolute alcoholic potassium hydroxide (20 c.c.) and the solution refluxed for four hours. As much alcohol as possible was then removed under reduced pressure by heating on a boiling water-bath. Water (15 c.c.) was added when a part of the solid dissolved and a part remained undissolved. The whole

of the mixture was acidified with hydrochloric acid and then directly taken up in ether. The ether solution was extracted thrice with 10 c.c. portions of 5% aqueous sodium carbonate. On acidifying the combined carbonate extract the ketone was obtained which separated as yellowish spear-head shaped crystals from alcohol and melted at 161–62°. Yield 0·4 g. (Found: C, 66·6; H, 5·5. $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·5%). It gave a red colour with alcoholic ferric chloride. The ether solution left after the extraction with carbonate was washed with water and dried over anhydrous sodium sulphate. On distilling off ether, a colourless solid was left behind. It was crystallised from excess of alcohol when a small quantity of a sparingly soluble product separated (80 mg.) as colourless rectangular plates and tablets melting at 203–05°. It gave a bluish violet colour with ferric chloride and was sparingly soluble in aqueous sodium hydroxide. It agreed in its properties with 5-hydroxy-6: 7-dimethoxy isoflavone described later and a mixed melting point with that sample was undepressed.

(*b*) *By fission of* 2-*methyl*-5-*hydroxy*-7: 8-*dimethoxy isoflavone* (XVI).—2-Methyl-5-hydroxy-7: 8-dimethoxy isoflavone (0·5 g.) was heated with 10 c.c. of 8% absolute alcoholic potassium hydroxide for four hours and the product worked up as in the previous case. The crystallised product was identical with the ketone sample described above and the mixed melting point was undepressed. Yield 0·2 g.

5-*Hydroxy*-6: 7-*dimethoxy isoflavone* (*X*)

Pulverised sodium (0·5 g.) and a solution of 2: 6-dihydroxy-3: 4-dimethoxy-phenyl-benzyl ketone (0·5 g.) in dry ethyl formate (5 c.c.) were employed. The product crystallised from ethyl acetate as colourless rectangular plates and tablets melting at 203–05°. Yield 0·3 g. (Found: C, 68·4; H, 5·1; $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%). It was found to be different from 5-hydroxy-7: 8-dimethoxy isoflavone in colour reactions and the mixed melting point was depressed considerably. The colour with alcoholic ferric chloride was bluish violet.

Using acetic anhydride and pyridine 5-acetoxy-6: 7-dimethoxy isoflavone was prepared and it crystallised from alcohol as colourless aggregates of long needles melting at 121–23° (Found: C, 67·2; H, 4·9; $C_{19}H_{16}O_6$ requires C, 67·0; H, 4·7%).

5: 6: 7-*Trimethoxy isoflavone* (*XII*)

5-Hydroxy-6: 7-dimethoxy isoflavone (0·3 g.) was refluxed in dry acetone (70 c.c.) with dimethyl sulphate (0·15 c.c.) and anhydrous potassium carbonate (1 g.) for sixteen hours. The potassium salts were filtered off and

washed with hot acetone. On distilling off the acetone from the filtrt e a colourless solid was obtained. Crystallisation from alcohol yielded the methyl ether as colourless rhombic prisms melting at 165–66°. Yield 0·15 g. (Found: C, 65·8; H, 5·8; $C_{18}H_{16}O_5$ requires C, 65·5; H, 5·4%). It did not dissolve in cold aqueous sodium hydroxide and did not give any colour with ferric chloride. The mixed melting point with the isomeric 5:7:8-trimethoxy isoflavone is considerably depressed.

5:6:7-*Trihydroxy isoflavone* (*XI*)

An acetic anhydride solution of 5-hydroxy-6:7-dimethoxy isoflavone (0·3 g. in 2 c.c.) was treated with cooling with hydriodic acid (sp. gr. 1·7, 6 c.c.) and the mixture heated on an oil-bath at 140–45° for two hours. It was then cooled and diluted with sulphurous acid. The bright yellow solid that separated was filtered, washed with water and crystallised from alcohol when it separated as yellow micaceous aggregates of thin rectangular plates melting at 282–83° (decomp.). Yield 0·15 g. (Found: C, 66·1; H, 4·0; $C_{15}H_{10}O_5$ requires C, 66·6; H, 3·7%). With ferric chloride it gave an olive green colour which changed to deep brown when excess was added. With sodium hydroxide solution it gave orange red colour which changed to brownish red, violet and finally blue.

5:6:7-Triacetoxy isoflavone was made by the acetic anhydride-pyridine method. It crystallised from alcohol as colourless narrow rectangular plates melting at 185–86°. (Found: C, 63·3; H, 4·0; $C_{21}H_{16}O_8$ requires C, 63·6; H, 4·0%); see Karmarkar *et al.*[12]

2-*Methyl*-5-*hydroxy*-6:7-*dimethoxy isoflavone* (*XIV*)

(1) 2:6-Dihydroxy-3:4-dimethoxy-phenyl-benzyl ketone (0·5 g.) was mixed with fused sodium acetate (0·5 g.) and heated with acetic anhydride (5 c.c.) under reflux in an oil-bath at a temperature of 170–80° for twelve hours. The contents were cooled and poured into crushed ice (30 g.) and left overnight. The slightly brownish product was filtered and crystallised from alcohol when 2-methyl-5-acetoxy-6:7-dimethoxy isoflavone separated as colourless rhombohedral prisms melting at 193–94°, yield 0·2 g. (Found: C, 67·5; H, 5·1; $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1%).

2-Methyl-5-acetoxy-6:7-dimethoxy isoflavone (0·1 g.) was boiled with 10 c.c. of 4% sodium hydroxide for 10 minutes. The solution was filtered hot to remove undissolved impurities, cooled well and acidified with hydrochloric acid. The product was taken up in ether and after drying the ether solution over anhydrous sodium sulphate the isoflavone was recovered by evaporation. It crystallised from alcohol as aggregates of colurless stout

prismatic rods melting at 145–46°. It gave blusih violet colour with alcoholic ferric chloride. It was identical with 2-methyl-5-hy lroxy-6 : 7-dimethoxy isoflavone described below.

(2) 2-Methyl-5 : 6 : 7-trimethoxy isoflavone[1] (50 mg.) was refluxed with concentrated hydrochloric acid (2 c.c.) for fifteen minutes. It was then diluted with water (10 c.c.) and the colourless solid that separated was filtered and washed with water. When crystallised from alcohol it separated as colourless stout prismatic rods melting at 145–46°. It gave a bluish violet colour with alcoholic ferric chloride. (Found: C, 69·6; H, 5·4; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%).

Summary

Using the more easily accessible 5 : 7 : 8-trihydroxy derivatives of isoflavones a convenient method has been worked out for the synthesis of 5 : 6 : 7-trihydroxy derivatives. It consists in the alkali fission of 5-hydroxy-7 : 8-dimethoxy isoflavone and its 2-methyl derivative to yield 2 : 6-dihydroxy-3 : 4-dimethoxy-phenyl-benzyl ketone. This ketone on treatment with ethyl formate and sodium yields 5-hydroxy-6 : 7-dimethoxy isoflavone. Vigorous acetylation of the ketone using acetic anhydride and sodium acetate yields 2-methyl-5-hydroxy-6 : 7-dimethoxy isoflavone which is compared with an authentic sample prepared by an independent method. 5-Hydroxy-7 : 8-dimethoxy isoflavone yields a small quantity of 5-hydroxy 6 : 7-dimethoxy isoflavone during alkali fission.

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APPLICATION OF LENNARD-JONES DEVONSHIRE EQUATION OF STATE TO DETONATION OF PETN

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Abstract

Kirkwood's extension of Lennard-Jones Devonshire model for liquids, to multicomponent fluid mixtures, has been used to find out the various parameters of detonation of pentaerythritol tetranitrate (PETN), for various loading densities. The exponent of the law of adiabatic expansion of hot dense products has been determined.

1. Introduction

1.1. The products of detonation of solid explosives form a mixture of highly imperfect gases. The investigation of the properties of these gases is connected with the solution of the configurational integral. One of the methods of solution is to split up the integral into sub-integrals (called the cluster integrals), their number depending on the degree of imperfection of the gases under consideration, and to evaluate them individually, assuming a certain law of molecular interaction. This method leads to a state equation as a series in terms of volume (or pressure). There are many successful investigations of the detonation of solid explosives, based on more or less this method of solution. An alternative to this procedure is based on the analogy of a highly imperfect gas to a liquid. In a liquid each molecule moves in a resultant field due to others. The correct description of the behaviour of liquids by distribution functions, though within the framework of Statistical Mechanics, is rather a difficult trek, and hence an approach based on intuitively plausible models, admitting of a straightforward numerical solution, has been more patronized instead. The cell model is quite a popular one. Any particular molecule is supposed to be encaged inside a cell of volume equal to the available volume per molecule. The energy of this molecule at any point inside the cell, due to the other surrounding molecules, is calculated assuming a certain law of molecular force. This energy will depend on its position within the cell. But if it is replaced by a value averaged out for all positions it leads to a smoothed potential model of a liquid. On the basis of this model Cottrell and Paterson[1]

worked out successfully the detonation properties of O_2 balanced explosive PETN, finding out and suitably adjusting the smoothed potential, from calculations on H_2 molecule ion.

1.2. Lennard-Jones and Devonshire[2] (LJD) took into account the variation of the potential inside the cell, and regarded the cell to be a sphere of radius, equal to the average distance between neighbours; the number of immediate as well as successive neighbours being determined on the assumption of a face centred cubic packing. Proceeding along these lines they worked with fair amount of success, the critical constants of various gases. The degree of success obtained made Kirkwood[3] place their theory on a firm footing, by deriving it from statistical mechanical considerations. He showed that it was the first approximate solution of a general set of integral equations, obtained under clearly defined assumptions, from well known precepts of Statistical Mechanics. He[4] later extended the theory to multicomponent fluid mixtures, deriving a state equation, suitable for the investigation of properties of solutions. The application of these results to the detonation of solid explosives has been envisaged by Ficket and Wood,[5] who have extended the tables of relevant functions in the range of interest. The present is an attempt to make use of Kirkwood's approach, to investigate the properties of PETN.

2. The State Equation and the Equilibrium Constant

2.1. The basic equation of state is given by

$$p = \frac{n\mathrm{RT}}{v}\left[1 + 4 \times \frac{12\bar{\epsilon}}{\mathrm{RT}}\left\{\left(\frac{\bar{v}^\circ}{v}\right)^4 \frac{g_l}{\mathrm{G}} - \left(\frac{\bar{v}^\circ}{v}\right)^2 \frac{g_m}{\mathrm{G}}\right\} + \frac{12\,\bar{\epsilon}}{\mathrm{RT}}\left\{2{\cdot}0218\left(\frac{\bar{v}^\circ}{v}\right)^4 - 2{\cdot}4090\left(\frac{\bar{v}^\circ}{v}\right)\right\}\right] \tag{1}$$

$$\bar{v}^\circ = \left[\frac{\sum_{i,l=1}^{r} x_i x_l \epsilon_{il} v_{il}{}^{\circ 4}}{\sum_{i,l=1}^{r} x_i x_l \epsilon_{il} v_{il}{}^{\circ 2}}\right]^{\frac{1}{2}} \tag{1 a}$$

$$\bar{\epsilon} = \frac{\left[\sum_{i,l=1}^{r} x_i x_l \epsilon_{il} v_{il}{}^{\circ 2}\right]^2}{\sum_{i,l=1}^{r} x_i x_l \epsilon_{il} v_{il}{}^{\circ 4}} \tag{1 b}$$

$$v_{il}{}^\circ = n a_{il}{}^3 \tag{1 c}$$

x_i, etc., are mole fractions, ϵ_{il} being the minimum of potential energy between a pair of molecules, and a_{il} the distance, at which this energy is minimum.

The form of molecular interaction assumed is the well-known 6–12 potential, namely,

$$\epsilon = 4\,\epsilon_{il}\left[\left(\frac{a_{il}}{r}\right)^{12} - \left(\frac{a_{il}}{r}\right)^{6}\right] \tag{2}$$

We assume

$$\epsilon_{il} = (\epsilon_{ii}\,\epsilon_{ll})^{\frac{1}{2}} \qquad a_{il} = \frac{a_{ii} + a_{ll}}{2}$$

g_l, g_m and G are given by

$$g_l = \int_0^{.30544} y^{\frac{1}{2}}\,\mathrm{L}(y)\exp(-\beta \mathrm{W})\,\mathrm{d}y$$

$$g_m = \int_0^{.30544} y^{\frac{1}{2}}\,\mathrm{M}(y)\exp(-\beta \mathrm{W})\,dy$$

$$\mathrm{G} = \int_0^{.30544} y^{\frac{1}{2}}\exp(-\beta \mathrm{W})\,dy$$

where $\mathrm{L}(y)$ and $\mathrm{M}(y)$ are given by

$$\mathrm{L}(y) = l(y) + \frac{1}{128}\,l(y/2) + \frac{2}{729}\,l(y/3)$$

$$\mathrm{M}(y) = m(y) + \frac{1}{6}\,m(y/2) + \frac{2}{27}\,m(y/3)$$

$$l(y) = (1 + 12\,y + 25{\cdot}2\,y^2 + 12\,y^3 + y^4)(1 - y)^{-10} - 1$$

$$m(y) = (1 + y)(1 - y)^{-4} - 1$$

$$y = \left(\frac{r}{a}\right)^2 \qquad \text{and}$$

$$\mathrm{W} = 12\,\tilde{\epsilon}\left\{\left(\frac{\overset{\circ}{\ }}{v}\right)^4 \mathrm{L}(y) - 2\left(\frac{\overset{\circ}{v}}{v}\right)^2 \mathrm{M}(y)\right\}$$

2.2. PETN being an oxygen balanced explosive, its products are mainly determined by the water gas equilibrium (assuming that no nitrogen compounds are formed). In view of the above state equation we have

$$\frac{\beta\gamma}{\alpha\delta} = \mathrm{K} \times \exp\left[\sum_{i=\alpha}^{\delta}\sum_{l=\alpha}^{\delta} x_i x_{il}\,12\left\{\left(2{\cdot}4090 + 4\,\frac{g_m}{\mathrm{G}}\right)\left(\frac{v_{il}^{\circ}}{v}\right)^2 - \left(1{\cdot}0109 + 2\,\frac{g_l}{\mathrm{G}}\right)\left(\frac{v_{il}^{\circ}}{v}\right)^4\right\}\right] \tag{3}$$

where K is the ideal equilibrium constant for the water gas reaction, and α, β, γ, δ are the number of gm. moles of CO_2, CO, H_2O and H_2 respectively; in the first sigma this being understood that α and δ are negative. With the help of (1 *c*) (3) becomes

$$\frac{\beta\gamma}{a\delta} = \mathrm{K} \times \exp\left[47{\cdot}882\left(2{\cdot}4090 + 4\frac{g_m}{\mathrm{G}}\right)\sum_{i=a}^{\delta}\sum_{l=a}^{\delta} n_l \frac{\epsilon_{il} a^{\circ}{}_{il}{}^{6}}{\mathrm{T}v^2} - 2{\cdot}1016 \times 10^3\left(1{\cdot}0109 + 2\frac{g_l}{\mathrm{G}}\right)\sum_{i=a}^{\delta}\sum_{l=a}^{\delta} \frac{n_l\, \epsilon_{il}\, a^{\circ}{}_{il}{}^{12}}{\mathrm{T}v^4}\right] \tag{3 a}$$

3. Choice of the Parameters of the Potential

The parameter ϵ_{il} and a_{il} used for the potential given by (2), for CO_2, CO, N_2 and H_2 are those recently determined by Hirschfelder *et al.*[6] The selection of these parameters for H_2O raises some difficulty. Corner[7] has made use of a potential found out by Hirschfelder *et al.*[8] for water molecule, to determine its second virial coefficient up to 4000° K. The potential of equation (2) leads to the value of the second virial coefficient given by

$$\left.\begin{aligned} \mathrm{B} &= b_0\, \mathrm{F}\left(\frac{\epsilon_{ii}}{\mathrm{KT}}\right) \\ b_0 &= \frac{2\pi}{3} a_{ii}{}^3 \end{aligned}\right] \tag{4}$$

The function of $\mathrm{F}\left(\frac{\epsilon_{ii}}{\mathrm{K\,T}}\right)$ has been evaluated by Lennard-Jones[9] from 1500–5000° K. Finding the value of the second virial coefficient upto 5000°, by extrapolation, from Corner's data it is possible with the help of equation (4), to fit the parameters of spherical potential, to the values of the second virial coefficient thus obtained. Those giving a best fit between 4000° and 5000° K are

$$\frac{\epsilon_{ii}}{\mathrm{K}} = 350^{\circ}\ \mathrm{K}\ ; \qquad a_{ii} = 2{\cdot}56\ \text{Å}$$

4. Determination of the Velocity of Detonation

3.1. The first step in the determination of the detonation velocity consists in the maping out the Hugoniot curve in p and v. given by the equation

$$\mathrm{E} - \mathrm{H} = \tfrac{1}{2}\, p\,(v_0 - v) \tag{5}$$

in which E is the internal energy of the products, H the heat of the reaction, v_0 the sp. volume of the explosive, p and v the pressure and volume in the detonation wave front. The latter are determined from the point of contact of the tangent from the point representing the initial conditions, to the curve. Then the detonation velocity D is given by

$$\mathrm{D} = v_0 \sqrt{\frac{p}{v_0 - v}} \tag{6}$$

By virtue of equation (1) we have

$$E = \Sigma ni\, E_i + n \times 12\, \bar{\epsilon} \left[\left(\frac{\bar{v}^\circ}{v} \right)^4 \left(\frac{g_l}{G} + 0{\cdot}50545 \right) - \left(\frac{\bar{v}^\circ}{v} \right)^2 \left(\frac{2g_m}{G} + 1{\cdot}2045 \right) \right] \tag{7}$$

E_i, etc., being the temperature dependent part of the internal energy of the gases, and is available from tables of Lewis and Elbe.[10]

4.2. In order to draw the curve of equation (5) consistent values of $\bar{v}^\circ$ and $\bar{\epsilon}$ have to be found out. The method of evaluating them is that of successive approximations, starting with the one, corresponding to the value of K for perfect gas condition. From the value of p and E obtained from the final value of $\bar{v}^\circ$ and $\bar{\epsilon}$, it is possible by equation (5) to find out the value of v_0, to which a certain assumed value of v corresponds, till the right value corresponding to a particular loading density ρ_0 is found out. This process repeated at different temperatures enables the curve to be drawn.

4.3. Working along these lines the value of the detonation velocity D at a loading density $\rho_0 = 1{\cdot}25$ gm./c.c., came out to be 8100 met./sec., as compared to the experimental value of 6700 met./sec. In the problem under investigation (*i.e.*, detonation of O_2 positive explosive involving no change in the total number of gm. moles of the products, with pressure or temperature) $\bar{v}^\circ$ and $\bar{\epsilon}$ remain sensibly constant in a fairly wide range of volume and temperature. The above value of the detonation velocity was calculated with $\bar{v}^\circ = 321$ c.c. and $\frac{\bar{\epsilon}}{K} = 125^\circ$ K. Kirkwood's analysis applies essentially to cells of equal size, which places a limit on the molecular sizes of the components forming the mixture, the properties of which can be investigated by this equation of state. This error in the calculated detonation velocity, seems to be due to large difference in the molecular size of the gases forming the detonation products. If however we regard the mixture, as a single gas of molecular diameter equal to the average diameter of the products, we have

$$a_{ii} = a_{il} = a_{ll} \ldots\ldots\ldots = \frac{\sum_{i,l=1}^{r} a_{il}}{r}$$

$$\bar{v}^\circ = v_{ii}^\circ = v_{ll}^\circ \ldots\ldots\ldots = n \left(\frac{\sum_{i=l=1}^{r} a_{il}}{r} \right)^3$$

and

$$\bar{\epsilon}^{\circ} = \frac{\left[\sum_{i=l=1}^{r} x_i x_l \epsilon_{il}\right]^2}{\sum_{i,l=1}^{r} x_i x_l \epsilon_{il}}$$

On the basis of this assumption $\bar{v}^{\circ} = 250$ c.c. and $\bar{\epsilon}/K = 125°$. The various parameters of detonation calculated from these values of $\bar{v}^{\circ}$ and $\bar{\epsilon}$, compared to solutions by other authors are tabulated below.

TABLE I

Loading density ρ_0 g./c.c.	Calculated velocity D met./sec.	Experimental velocity D met./sec.	Temperature T° K				Pressure P 10^5 atmospheres			
			LJD method	Cottrell and Paterson[1]	Paterson[11]	Jones[12]	LJD method	Cottrell and Paterson	Paterson[11]	Jones[12]
1·00	5671	5550	4900	3650	5150	4400	·85	·88	·74	·86
1·50	7474	7600	4700	3280	5340	..	1·96	2·25	1·88	..
1·72	8505	8300	4420	1950	..	..	2·56	2·85	..	..

This approximation seems to satisfy the requirements of an equation of state applicable to the detonation products of solid explosives.

5. Discussion

The calculations by Cottrell and Paterson,[1] and by Paterson[11] mentioned above are the result of direct approaches (*i.e.*, the solution of D *versus* ρ has been worked out on the basis of a known equation of state) while those by Jones[12] are based on an inverse one (*i.e.*, the parameters of detonation, as well as those of an assumed equation of state, have been calculated from the experimentally known relation between detonation velocity and loading density). Comparison of the solution by LJD method, with that of Cottrell and Paterson,[1] and Paterson[11] reveals that the same amount of energy (for a particular loading density, the heat of the reaction may be assumed to be the same in all solutions) gives the least temperature and maximum pressure in the former, greatest temperature and least pressure in the latter, while the pressure and temperatures found by LJD method are intermediate between the two. This is so because Paterson[11] proceeds from a state equation of the form $pv = RTf(v)$, which gives rise to no interaction term in the expression for the internal energy, and hence results in a higher temperature. For the same reason the temperature is higher for a larger loading density. The solution of Cottrell and Paterson[1] depends as mentioned earlier, on

smoothed potential cell model, in which only the repulsive energy is considered. It takes into account the electronic redistribution in molecules at high densities, and the consequent decrease in polarisability, and hence neglects the attractive energy. An appreciable amount of the heat evolved is used up in overcoming the repulsive forces, and therefore gives lower temperature. At larger loading densities the effect of repulsive forces is more pronounced, and hence is responsible for giving lower temperatures for higher loading densities. In LJD method on the other hand both attractive and repulsive energies are comparable, as will appear from Table II, for in this case the polarizability and the ionization potential, etc., are absorbed into a constant, whose change with density is not considered. The dependence of the energies on intermolecular distance alone is taken into account.

TABLE II

Volume Å^3	Attractive Energy 10^{-12} eargs	Repulsive Energy 10^{-12} eargs
135	−·0194	·0007
104	−·0327	·0018
35	−·2888	·1399
20	−·8845	1·321
11	−2·924	14·34

The pressures obtained by Paterson[11] are very much low so much so that they mask the effect of higher temperature supposed to be prevailing there. The reason for this may be sought in the compressibility factor compiled in Table III. The compressibility factor is a measure of the slope of the curve of $\log \int_0^w e^{-W/KT} dv$ (W being the energy of a molecule in the field

TABLE III

pv/nRT

T° K	2,500			3,750		
	LJD method	Cottrell and Paterson[1]	Paterson[11]	LJD method	Cottrell and Paterson[1]	Paterson[11]
175	8·107	11·494	5·293	7·033	8·475	5·293
200	6·265	9·434	4·351	5·636	6·944	4·351

of others) against volume. Paterson's[11] results are based on a rigid sphere model, and therefore the curve referred to above is less steep, while in Cottrell and Paterson's solution, with a small increase in v, there is a considerable change in $\log \int_0^v e^{-W/KT} dv$ due to repulsive forces considered, resulting in a steeper curve and hence, large compressibility factor. In LJD solution, the slope lies in between, for it takes account of both attractive and repulsive energies.

As regards the results of Jones,[12] it is known that the information received regarding the state equation, by the inverse method, is very limited. It does not give the form of the equation applicable under those conditions of high temperature and pressure, but only enables certain arbitrary parameters, to be determined in an assumed equation of state. Jones[12] proceeds along a form $pv = RT + f(p)$, which gives rise to an interaction term in the internal energy. This enables the interaction energy to be determined, without any *a priori* assumptions, regarding molecular interaction. A formal comparison with direct solutions brings out that the attractive energy is not completely negligible as assumed by Cottrell and Paterson nor is it exactly given by LJD expression.

6. The Exponent of Adiabatic Law

The exponent of the adiabatic law of expansion of hot dense products may be determined by finding out the entiopy S of the products in the detonation wave front, and assuming it to be constant throughout. For $\rho_0 = 1{\cdot}0$ gm./c.c. S = ·67 K.cal./degree/gm. mole of PETN. If p and v are the values of pressure and volume at any instant during the process γ is given by

$$\gamma = -\frac{d \log p}{d \log v}$$

The results are tabulated below.

Temperature T° K	Pressure $P \times 10^{-10}$ dynes/cm.^{2}	Volume v c.c./gm. mole of PETN	γ
4900	·836	234	
			2·60
4700	·675	254	
			2·52
4500	·558	274	
			2·49
4300	·453	298	
			2·44
4100	·372	326	

The parameters of the state equation are valid only in a limited range of temperature and volume, and hence they do not permit the calculation of γ in the range except that given in the table. The values found agree reasonably with that found by other authors,[13, 14] specially with results of Jones and Miller[15] for TNT for $\rho_0 = 1{\cdot}0$ gm./c.c. They found that γ decreases with decrease in pressure. A similar trend is indicated in these results.

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NAPHTHOQUINONE SERIES

Part V. Reaction of 2 : 3–Dichloro–1 : 4–naphthoquinone with β–Ketoesters, Diethyl Malonate, Acetyl Acetone and Acetoacetanilide in Pyridine

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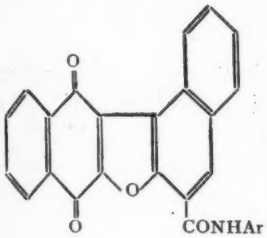
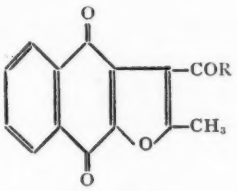
Synthesis of brazanquinone vat dyes of the type (II) by the condensation of 2 : 3-dichloro-1 : 4-naphthoquinone (I) with *o*-hydroxycarboxyarylides in pyridine was described in the previous communications.[1] The present work was initially undertaken with the view to prepare furanonaphthoquinone vat dyes, such as (III), starting from (I) and azoic coupling components containing a reactive methylene group. Condensation of (I) with the latter type of compounds in presence of sodium ethoxide leading to 3-chloro-2-substituted and 2 : 3-disubstituted 1 : 4-naphthoquinones has been described in the previous paper.[3] Ring closure of the latter gives deep coloured naphthindene[3] derivatives. Eistert[4] has likewise observed that



(II)



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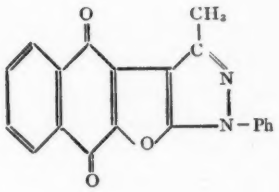
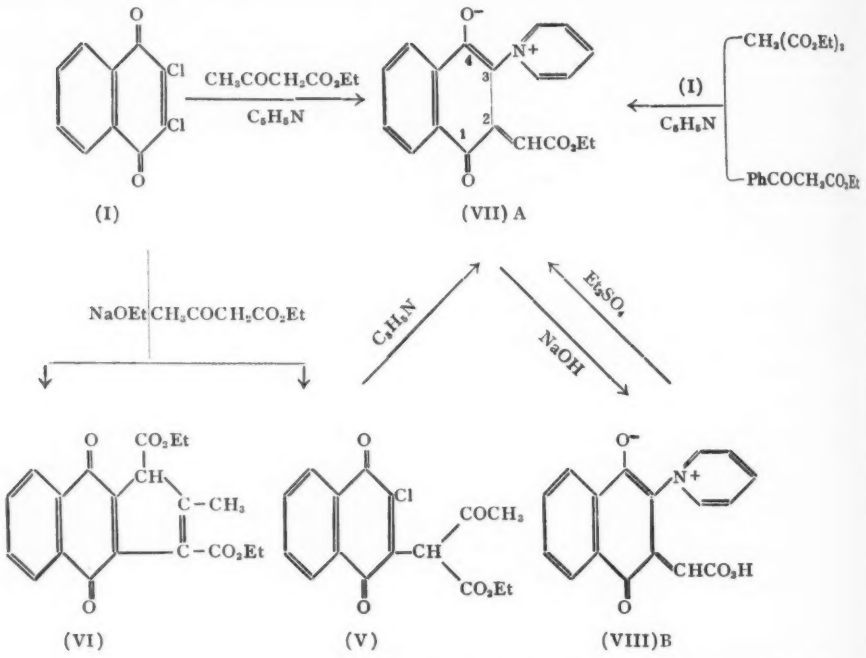


(IV)

R = Aryl, Alkyl, OEt or NHAr

reaction of (I) with 1-phenyl-3-methyl-5-pyrazolone in the presence of sodium ethoxide leads to an open chain 2 : 3-bis-pyrazolyl derivative. However, when the above condensation was carried out in pyridine, Eistert obtained the furanonaphthoquinone derivative (IV). It appeared likely therefore that the condensation of (I) with compounds containing a reactive methylene group in pyridine might lead to the desired furanonaphthoquinone derivatives. A brief account of the present work has already been reported by us recently[2] and the present paper gives further details.



Whereas reaction of (I) with ethylacetoacetate in the presence of sodium ethoxide gave (V) and (VI),[3] condensation in pyridine yielded a nitrogen-containing orange quinonoid compound (A). The latter is considered to be 1-keto-2-carboethoxymethylenyl-1 : 2-dihydronaphthalene-3-pyridinium-4-oxide (VII) on the basis of its properties, elementary composition and the following considerations:

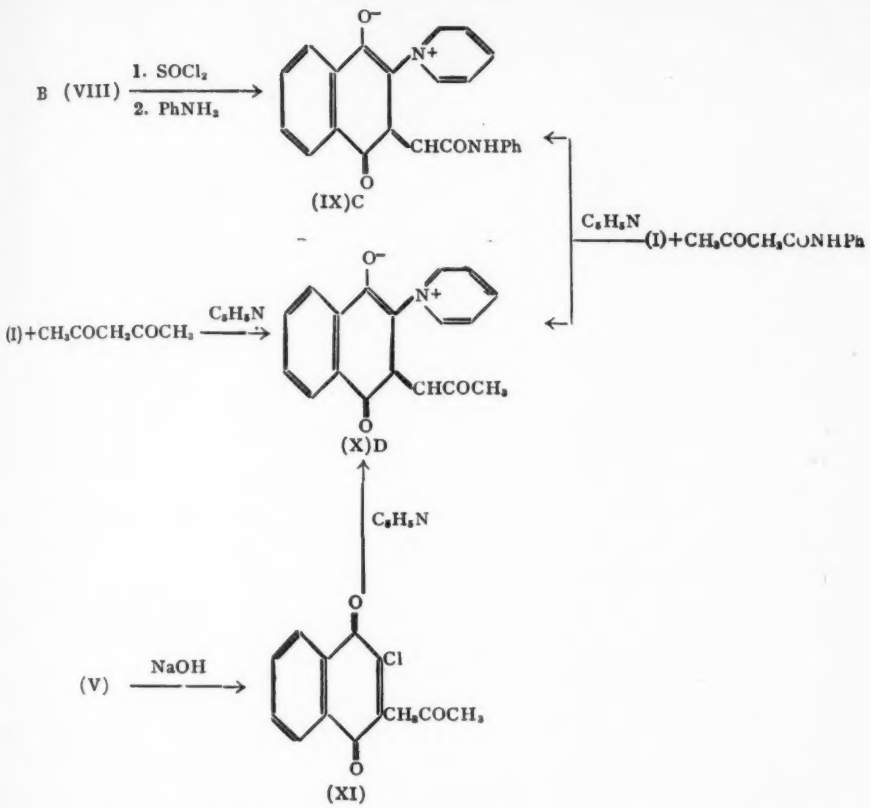
(1) (A) was also obtained by boiling (V) with pyridine.

(2) Hydrolysis of (A) with alcoholic sodium hydroxide gives an acid (B) showing the presence of an ester group in (A).

(3) Esterification of (B) gave back (A), confirming the presence of the carboethoxy group in (A).

(4) Acid (B) gave the anilide (C) through the acid chloride (using thionyl chloride).

(5) Condensation of diethyl malonate and ethyl benzoylacetate with (I) in pyridine gave (A).

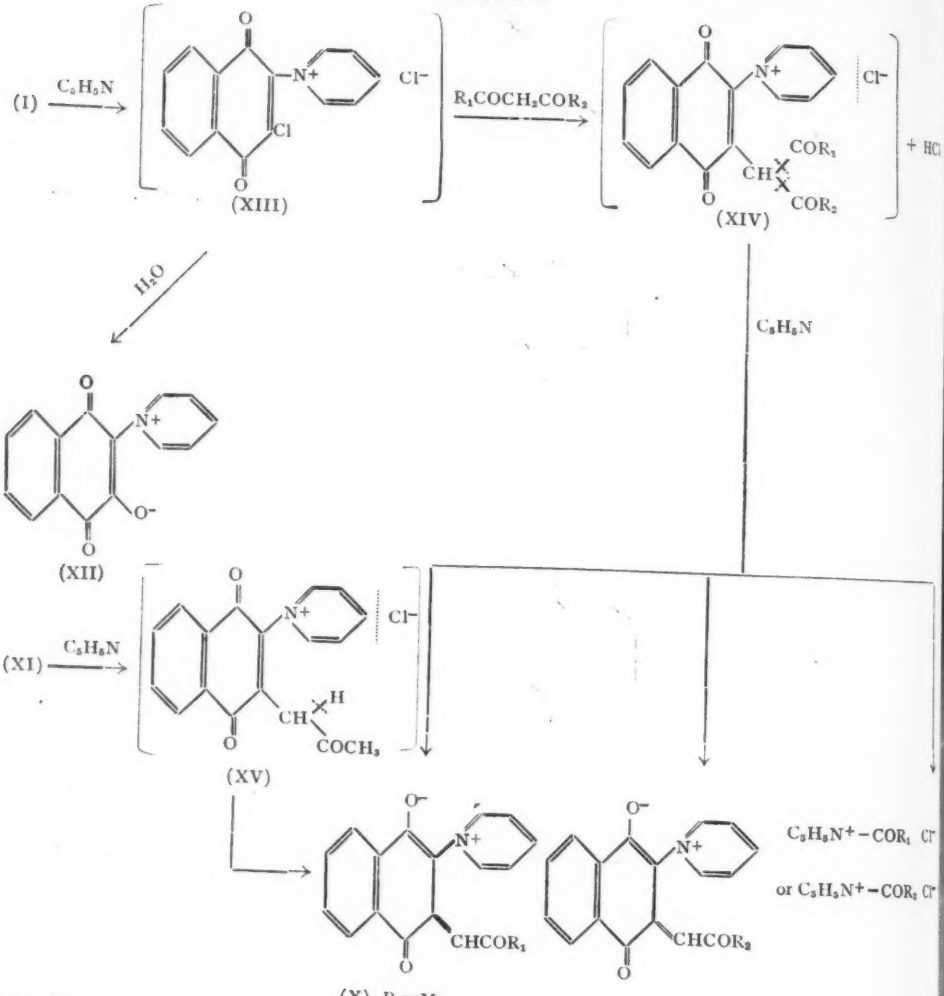


In view of the above facts, compounds (B) and (C) should be constituted as 1-keto-2-carboxymethylenyl-1 : 2-dihydronaphthalene-3-pyridinium-4-oxide (VIII) and 1-keto-2-carboxyanilidomethylenyl-1 : 2-dihydronaphthalene-3-pyridinium-4-oxide (IX) respectively. The reaction of acetoacetanilide with (I) in pyridine gave two products: (*a*) violet needles, m.p. 255°, and (*b*) a red crystalline product (D), m.p. 204–5°. The former proved to be identical with (C) obtained from (A) through the acid chloride. The product (D) was considered to be 1-keto-2-acetomethylenyl-1 : 2-dihydronaphthalene-3-pyridinium-4-oxide (X) on the basis of its elementary analysis and the following considerations:

(1) Condensation of (I) with acetyl acetone in pyridine gave (D).

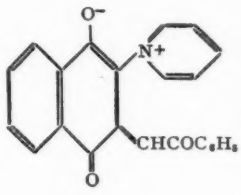
(2) Mild alkaline hydrolysis of (V) gave 2-acetonyl-3-chloro-1 : 4-naphthoquinone (XI), which on treatment with boiling pyridine gave (D).

CHART I



The synthesis of the above compounds is explicable on the basis of the reaction mechanism shown in Chart I. The synthesis of a "pyridinium anhydride" by the reaction of (I) with pyridine was first described by Ullmann and Ettisch,[5] who suggested that it was formed through an unstable

intermediate such as (XIII). Eistert[4] later suggested the pyridinium betaine structure (XII) to the above compound. In the reaction of (I) with ethyl acetoacetate also, (XIII) is probably formed and it then reacts with ethyl acetoacetate to give the intermediate compound, such as (XIV). The latter then undergoes fission in two directions leading to (X) and (VII). Simultaneous elimination of a chloride ion and $COCH_3$ or COR fragments probably takes place with the formation of the corresponding N-substituted pyridinium chlorides. The synthesis of (VII) from (V) is explicable on similar grounds. When (XI) is treated with pyridine, (XV) is probably formed and the latter then leads to (X) with the loss of hydrogen chloride which is taken up by pyridine present.

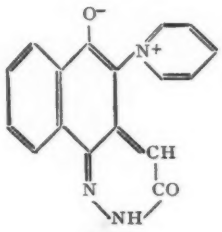


(XVI)

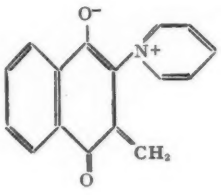
Further evidence in support of the above reaction mechanism was provided by the study of the reaction of (I) with diethyl malonate, ethyl benzoylacetate and acetyl acetone in pyridine. Reaction of diethyl malonate and ethyl benzoylacetate and (I) in pyridine gave (VII). Attempts to isolate (XVI), which may be expected to be formed in the condensation of ethyl benzoylacetate were unsuccessful. In the case of acetoacetanilide, however, both the products of fission, *viz.*, (IX) and (X), were isolated. The reaction of (I) with acetyl acetone gave (X) in good yield. Attempts to isolate N-acylpyridinium chlorides in the above condensations, were unsuccessful. This failure may, however, be due to the known instability of N-acylpyridinium chlorides.[6]

The possibility of the prior formation of (V), in the reaction of (I) with ethyl acetoacetate in pyridine and its subsequent condensation with pyridine to give the intermediate (XIV), was also considered. In order to test this possibility, attempts to synthesize (V) by condensation of (I) with ethyl acetoacetate in the presence of acid binding agents which do not react with (I), such as diethylaniline, were undertaken. These and other attempts to isolate (V) from the reaction of acetoacetic ester with (I) in pyridine, however, proved unsuccessful. These experiments give further support to the reaction mechanism suggested earlier.

Compounds (VII) to (X) are similar to the enol betaines of the indan-pyridinium series described by Stafford[7] and probably exist as resonance hybrids of several polar forms. The positive charge is probably fixed on the nitrogen atom whereas the negative charge may be located on several other atoms. The compounds described above have sharp and high melting points, with the exception of the acid (VIII) which melts with decomposition at 307–8°. Their stable nature is illustrated by (VII) which is unaffected by cold concentrated sulphuric acid, hot concentrated hydrochloric acid, a brief treatment with boiling 10% aqueous sodium hydroxide and reduction by alkaline hydrosulphite (brownish red vat) and subsequent reoxidation. The ester group in (VII) does not react with aniline in boiling toluene or with 50% aqueous hydrazine. Although the stability of the carboethoxy group indicates its participation in the polarization of (VII), it nevertheless reacts under vigorous conditions. Thus it is hydrolysed by boiling alcoholic alkali and reacts with boiling alcoholic 85% hydrazine hydrate. The reaction with the latter reagent led to a hydrazide which cyclized *in situ* to give the dihydropyridazone derivative (XVII). Compounds (IX) and (X) are also stable to reduction with hot alkaline hydrosulphite solution, but these and (VII) have no substantivity to cotton.



(XVII)

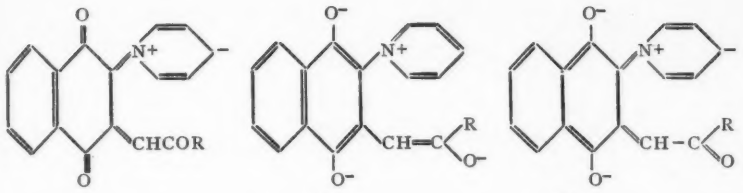


(XVIII)

In view of the decomposition of the acid (VIII) at its melting point, it was decarboxylated when 1-keto-2-methylenyl-1 : 2-dihydronaphthalene-3-pyridinium-4-oxide (XVIII) was obtained in almost quantitative yield. The latter represents the basic structure from which the above pyridinium oxides are derived.

Colour and vattability of the naphthoquinone pyridinium betaines

The deep colour of the above compounds can be explained on the basis of the combination of the extended conjugated system and the polar nature of the molecule and, in addition, contributing structures such as (*a*) which involve charge separation in the nitrogen-containing part of the molecule,



(*a*) (*b*) (*c*)

Although the above compounds do not contain a *p*-quinone grouping, they are nevertheless vattable probably due to the presence of a pair of carbonyl groups (one of which is in the naphthalene ring) connected by a conjugated chain which forms, in effect, a quinonoid system. A close parallel is the case of pyrimidanthrones[8] which contain one cyclic carbonyl group and are still vattable, on account of the resonance stabilization of the anion of the leuco compounds. The above pyridinium betaines, on reduction with alkaline hydrosulphite, probably give rise to an anion which is stabilised by resonance between structures such as (*b*) and (*c*).

In view of the known antimitotic activity[9] of certain naphthoquinones and their general physiological activity, the biological activity of the above and related compounds will be examined.

Experimental

1-*Keto*-2-*carboethoxymethylenyl*-1 : 2-*dihydronaphthalene*-3-*pyridinium*-4-*oxide* (*VII*)

2 : 3-Dichloro-1 : 4-naphthoquinone (I) (9·08 g.) was gradually added to a boiling solution of ethyl acetoacetate (5·2 g.) in pyridine (75 c.c.). The solution quickly changed its colour as follows: olive green→bluish black→brown→reddish brown. The mixture was then boiled under reflux for 3 hours and the clear solution was cooled to 0°. The dark brown sticky product which separated was collected, washed with a little ether and finally triturated with more ether (100 c.c.) before filtration. The brown crystalline residue (6·2 g.), m.p. 148–51°, was recrystallized (norit) from 95% alcohol (300 c.c.), when it gave lustrous orange brown elongated plates (4 g.), m.p. 154°, unaltered by further crystallization and purification by chromatography (Found: C, 70·6; H, 4·4; N, 4·7. $C_{19}H_{15}NO_4$ requires C, 71·0; H, 4·7; N, 4·4%). The ether washings on concentration gave another crop (0·3 g.) of the above product. A further quantity (1·5 g.) was obtained from the pyridine on keeping at 0° for 2 days (total yield 62·5%). Its solutions in benzene and ether are brownish red when concentrated and

yellow when dilute and show strong green fluorescence, whereas its solution in alcohol does not show fluorescence.

Preparation of (VII) from (V)

A mixture of (V) (2·0 g.) and pyridine (20 c.c.) was refluxed for 1½ hours. After gradually cooling to 0°, the mixture was filtered when a brick-red residue (0·7 g.) was obtained. After washing with alcohol and drying, the product, m.p. 145–55°, was extracted with hot benzene (30 c.c.). The orange coloured extract, after treating with norit and concentration, gave orange crystals, m.p. 154–55°; undepressed when mixed with (VII).

1-*Keto*-2-*carboxymethylenyl*-1:2-*dihydronaphthalene*-3-*pyridinium*-4-*oxide*(*VIII*)

An aqueous alcoholic solution (30 c.c. of 75% alcohol) of sodium hydroxide (1·0 g.) was added gradually to a boiling suspension of the ester (VII) (2·5 g.) in alcohol (130 c.c.). Hydrolysis took place almost immediately with the separation (in about 10 minutes) of a pink coloured gelatinous precipitate of the sodium salt of the acid (VIII). Alcohol was then distilled under reduced pressure and the sodium salt was dissolved in boiling water and treated with concentrated hydrochloric acid. The carboxylic acid (VIII), which precipitated on cooling, was collected, washed acid-free (Congo Red) and dried. The crude acid, m.p. 275–80° (decomp.), was crystallized from acetic acid when it gave violet needles (2·0 g.), m.p. 307–8° (decomp.) (Found: C, 69·3; H, 3·5; N, 5·2. $C_{17}H_{11}NO_4$ requires C, 69·6; H, 3·8; N, 4·8%).

Esterification of the acid (VIII)

A mixture of the acid (VIII) (0·1 g.), diethyl sulphate (0·4 c.c.), anhydrous potassium carbonate (1·0 g.) and dry acetone (20 c.c.) was refluxed for 20 hours. The orange-coloured acetone solution was filtered and poured into water. The precipitate (50 mg.), m.p. 140–50°, was crystallized (norit) from alcohol when it gave orange-brown plates, m.p. 154–55°, undepressed when mixed with (VII).

1-*Keto*-2-*carboxyanilidomethylenyl*-1 : 2-*dihydronaphthalene*-3-*pyridinium*-4-*oxide* (*IX*) *and* 1-*keto*-2-*acetomethylenyl*-1 : 2-*dihydronaphthalene*-3-*pyridinium*-4-*oxide* (*X*)

A mixture of (I) (1·5 g.), acetoacetanilide (0·85 g.) and pyridine (10 c.c.) was refluxed for 2 hours. After cooling, the mixture was filtered and the crystalline residue was washed with alcohol and ether and dried. The product (0·75 g.), m.p. 239–42°, on recrystallization from pyridine, gave (IX)

as violet-needles, m.p. 255° (Found: C, 74·7; H, 4·1; N, 7·7. $C_{23}H_{16}N_2O_3$ requires C, 75·0; H, 4·4; N, 7·6%).

Dilution of the pyridine mother-liquor with alcohol gave a red coloured precipitate (0·15 g.), m.p. 194–95°, which after crystallization from aqueous pyridine gave (X) as red needles, m.p. 204° (Found: C, 74·6; H, 4·0; N, 5·2. $C_{18}H_{13}NO_3$ requires C, 74·2; H, 4·4; N, 4·8%).

Conversion of (VIII) to (IX)

The acid (VIII) (0·6 g.) was refluxed with thionyl chloride (6·0 c.c.) for 40 minutes when a red coloured product separated. The excess thionyl chloride was removed by distillation under reduced pressure. Dry benzene (15 c.c.) was added and the solvent was removed under reduced pressure. This operation was repeated four times in order to ensure complete removal of thionyl chloride. The residue (acid chloride) was then boiled in dry benzene (50 c.c.) and a solution of aniline (0·6 g.) in benzene (10 c.c.) was added. The colour of the solution quickly changed from orange to deep violet and a crystalline residue separated out gradually. The mixture was refluxed for 5 hours and filtered hot. The product was washed with benzene, dried (0·32 g.) and crystallized from pyridine when it gave violet needles, m.p. 255°. The m.p. of the product was undepressed when mixed with (IX) described above. The filtrate on cooling gave a second crop of red violet needles (0·27 g.), m.p. 252–55°.

3-*Chloro*-2-*acetonyl*-1 : 4-*naphthoquinone* (*XI*)

A fine powder of (V) (1·0 g.) was gradually added to ice-cold (5°) aqueous sodium hydroxide (20 c.c. of 5%) under stirring. After leaving for 15 minutes the initial blue colour of the solution gradually changed to brown. Dilute hydrochloric acid (15 c.c, 1 : 2) was added dropwise to the clear solution during 15 minutes keeping the solution vigorously stirred and cooled at 5°. The mixture finally became yellow and a granular precipitate separated. The latter was separated, washed free from acid and crystallized (norit) from 95% alcohol (15 c.c.) when it gave yellow needles, m.p. 147–48° (yield, 0·3 g.), raised to 150–51°, by recrystallization from the same solvent (Found: C, 63·1; H, 3·9. $C_{13}H_9ClO_3$ requires C, 62·8; H, 3·6%).

Compound (XI) was treated with boiling pyridine for 1 hour. Chromatographing a benzene solution of the reaction product on alumina led to the isolation of a red crystalline substance, m.p. 200–5°, which was found to be identical with (X).

Reaction of (I) with diethyl malonate in pyridine

A mixture of (I) (2·27 g.) and dry pyridine (10 c.c.) was gently heated for 15 minutes on a water-bath when a brown resinous solid separated out. Diethyl malonate (2·0 g.) was then added, followed by more pyridine (2 c.c.). The mixture was refluxed for 1½ hours and cooled in ice when a brownish residue (0·9 g.) was obtained, which was identified as the betaine (XII). The mother-liquor was extracted with ether (250 c.c.), the extract washed with dilute hydrochloric acid, water, dried and solvent removed by distillation. The brown coloured residue (0·2 g.) was found to be identical with (VII).

Reaction of (I) with ethyl benzoylacetate in pyridine

A mixture of (I) (4·5 g.) and dry pyridine (20 c.c.) was heated on water-bath as above. Ethyl benzoylacetate (7·6 g.) was then added and the mixture was refluxed for 2 hours. The brown coloured crystalline product (1·0 g.), m.p. 147–49° which separated on cooling, was collected and re-crystallized from alcohol when it gave a crystalline substance which was found to be identical with (VII). The mother-liquor on prolonged standing gave a second crop of the reaction product (1·0 g.).

Reaction of (I) with acetyl acetone in pyridine

A mixture of (I) (2·27 g.) and dry pyridine (10 c.c.) was heated on a water-bath as in the above experiment. Acetyl acetone (1·5 g.) was added and the mixture was refluxed for 2 hours. After cooling to room temperature, the mixture was filtered and the residue (1·25 g.), m.p. 195–200°, was crystallized from benzene when it gave red needles, m.p. 204–5°; undepressed when mixed with (X) described above.

Synthesis of (XVII) from (VII)

A mixture of (VII) (1·0 g.), 85% aqueous hydrazine hydrate solution (2·0 c.c.) and absolute alcohol (25 c.c.) was refluxed for 6 hours. The solution turned red gradually and a yellow product separated out, which was collected and washed with alcohol. The product (0·95 g.) after three crystallizations from nitrobenzene gave silky yellow needles of (XVII), which did not melt up to 300° (Found: C, 70·7; H, 3·7; N, 14·4. $C_{17}H_{11}N_3O_2$ requires C, 70·6; H, 3·8; N, 14·5%).

1-Keto-2-methylenyl-1 : 2-dihydronaphtl ene-3-pyridinium-4-oxide (XVIII)

The acid (VIII) (0·24 g.) and copper bronze (5 mg.) were refluxed in quinoline (3·0 c.c.) for 1½ hours. The mixture was filtered and the residue was washed with quinoline (2 c.c.). The quinoline extract on cooling to 0° deposited short orange needles which were collected and washed with benzene

(20 c.c.). Yield 50 mg., m.p. 236°. Recrystallization from benzene gave minute orange needles, m.p. 240° (Found: C, 76·8; H, 4·0; N, 6·0. $C_{16}H_{11}NO_2$ requires C, 77·1; H, 4·4; N, 5·6%). Removal of benzene from the washings gave a further quantity (50 mg.) of the product, m.p. 235°. The quinoline mother-liquor on steam distillation gave another crop of the product (0·1 g.) (total yield 98%). The benzene solutions are yellow when dilute and orange red when concentrated and show strong green fluorescence.

Summary

The condensation of 2: 3-dichloro-1: 4-naphthoquinone (I) with compounds containing a reactive metnylene group in pyridine was studied. The reaction of (I) with ethyl acetoacetate in pyridine gave 1-keto-2-carboethoxymethylenyl-1: 2-dihydronaphthalene-3-pyridinium-4-oxide (VII). The corstitusion assigned to (VII) is supported by its alternative synthesis from (I) and diethyl malonate or ethyl benzoylacetate in pyridine. Hydrolysis of (VII) gave 1-keto-2-carboxymethylenyl-1: 2-dihydronaphthalene-3-pyridinium-4-oxide which was converted to 1-keto-2-carboxyanilidomethylenyl-1: 2-hydronaphthalene-3-pyridinium-4-oxide (IX) and 1-keto-2-methylenyl-1: 2-dihydronaphthalene-3-pyridinium-4-oxide.

The reaction of acetoacetanilide with (I) in pyridine gave (IX) and 1-keto-2-acetomethylenyl-1: 2-dihydronaphthalene-3-pyridinium-4-oxide. The latter was also synthesized from 2-chloro-3-acetonyl-1: 4-naphthoquinone and acetyl acetone by reaction of these substances with (I) in pyridine.

A reaction mechanism to account for the formation of the above compounds is suggested.

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THE THEORY OF ELASTICITY AND OF WAVE-PROPAGATION IN CRYSTALS FROM THE ATOMISTIC STANDPOINT

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Introduction

The earliest attempt to formulate the theory of elasticity on the basis of the discrete atomic structure of matter was due to Cauchy who, assuming central interactions between pairs of atoms of a homogeneous body, deduced his well-known relations among the elastic constants. Recent developments, however, have shown that a central force-scheme is inadequate to describe correctly the interatomic interactions in solids and that the Cauchy relations[1] are violated by many crystals. The later theory of Green has the merit of resulting directly in all the 21 independent elastic constants which have since then been found to be innately essential for an adequate description of the elastic behaviour of crystals in general.

There are two principal methods for determining the values of the elastic constants experimentally for crystals. The first is the static procedure in which the solid is subjected to external stress and the resulting deformation is measured. When the deformation is homogeneous, the elastic constants can be calculated from the stress-strain relations implied in Hooke's law. In the second one, which is the dynamic method, the velocities of propagation of specific types of waves are observed and the elastic constants are evaluated therefrom. It is essential in the latter procedure to restrict attention to waves of large wavelengths and low frequencies. For, waves inside crystals are dispersive and are of a much more general character than the ordinary elastic waves. The validity[2] of the elasticity theory will thus break down for stationary vibrations of high frequencies and it can be sustained only over those regions of the frequency spectrum wherein the frequencies of the waves vary inversely as their wavelengths. Conversely, as the long waves of the three acoustic branches satisfy this criterion, the elastic behaviour of crystals could be expected to be determined by these low frequency vibrations involving mass movements of their lattice cells. This enables one to write quantitative identities between the elastic constants

and the force constants of the atomistic theory. In the process of comparing the two theories, however, it is essential beforehand to reduce the mathematical framework of both the formulations to identical forms. Thus, it is necessary to set up as many equations in lattice theory as in the continuum theory, with their variables possessing identical significance and further to ensure that these two sets of equations are of the same form. When this condition is complied with, the scope and physical implications of both the formulations become identical and one can compare the two sets of equations to derive relations between the parameters involved in them.

It was shown by Born[3] that the macroscopic elastic properties of crystals could be deduced from an atomistic lattice theory in terms of a few parameters which are the force constants of the potential energy expression and the lattice constants. As this theory is based on the assumption of central forces, the problem was reconsidered again by Begbie[4] and Born,[4] using a general force scheme. By comparing the lattice equations of the long acoustic waves with the elastic wave equations, they obtained expressions for the elastic constants in terms of the force-constants. But, in spite of the use of a general force-scheme, these expressions still continue to hold good for central force systems only, as the validity of a symmetry relation used by them could be realised only for central interactions among the atoms. A second set of relations for the elastic constants were later given by Kun Huang.[5] Again, his theory also restricts the generality of the force-scheme by introducing new compatibility conditions among the force constants. Since the validity of these relations can be realised strictly for central force systems only, the results of Kun Huang also are not in general reliable.

It is shown in this paper that it is possible to derive an expression for the strain-energy function characterising the deformation of the lattice, from general dynamical considerations. This function is a quadratic in all the nine strain components, unlike the classical theory in which the deformation energy is a quadratic in the six strain components only. From the Lagrangian obtained in this way, the variational equations describing the nature of waves traversing the crystal can be written down and these are identical with the equations of Born and Begbie. But since these equations are not in the same mathematical form as the wave-equations of the elasticity theory, it is clearly not justifiable to identify these two sets of equations to obtain identities between the constants involved in them. Expressions for the elastic constants can nevertheless be derived by comparison, as the two strain energy functions assume the same form for irrotational strains or for homogeneous deformations. It is shown that the numerical values of the elastic constants calculated

from the expressions obtained in this way agree well with the experimental values for the case of diamond, whereas significant deviations from the experimental results arise from the relations derived by comparing directly the elastic wave equations with the lattice wave-equations of Begbie and Born.

The paper is divided into two parts. In Part I, the static method of finding the strain energy function for a general deformation is developed and expressions for the elastic constants are given in terms of the force constants. Part II deals with the propagation of acoustic waves inside crystals.

PART I. THE STATIC METHOD

I. The Deformation energy

We choose the state in which all the atoms of the crystal (assumed to be very large compared to the dimensions of its unit cell, but still finite) are at their lattice sites, as the zero configuration for the potential energy of the lattice. The total potential energy of the crystal for small nuclear displacements is then given by

$$2V = \sum_{xrs} \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\, q_{xrs}\, q_{y\rho\sigma} \tag{1}$$

where q_{xrs} denotes the displacement of the atom (r, s) from its equilibrium position. The equations of motion of the atoms of the cell (s) of the crystal are given by

$$-m_r \ddot{q}_{xrs} = \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\, q_{y\rho\sigma} \tag{2}$$

The force constants satisfy the following relations, which express the invariance conditions of the potential energy under pure translations.

$$\sum_{\rho\sigma} k^{y\rho\sigma}_{xrs} = 0 \qquad (x, y = x, y, z) \tag{3}$$

With the help of (3), we can rewrite (2) as

$$-m_r \ddot{q}_{xrs} = \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\,(q_{y\rho\sigma} - q_{yrs}) \tag{4}$$

The total force on the atom (r, s) in the x-direction is therefore a linear sum of the forces due to the displacements of its neighbours, the force exerted by the atom (ρ, σ) on (r, s) being equal to $\sum_y k^{y\rho\sigma}_{xrs}\,(q_{y\rho\sigma} - q_{yrs})$. The force constant $k^{y\rho\sigma}_{xrs}$ denotes the force on (r, s) in the x-direction due to (ρ, σ) per unit relative displacement of these two atoms parallel to the y-direction

The work done by (ρ, σ) on (r, s) is given by

$$\sum_{xy} k^{y\rho\sigma}_{xrs} (q_{y\rho\sigma} - q_{yrs}) q_{xrs} \qquad (5\,a)$$

Similarly the work done by (r, s) on (ρ, σ) is given by

$$\sum_{xy} k^{x\rho\sigma}_{yrs} (q_{yrs} - q_{y\rho\sigma}) q_{x\rho\sigma} \qquad (5\,b)$$

The sum of (5 *a*) and (5 *b*) gives twice the contribution of the atoms (r, s) and (ρ, σ) to the total intrinsic energy of the crystal in a potential field caused by the vibrations of the remaining atoms; it is equivalent to twice the mutual potential energy $V^{\rho\sigma}_{rs}$ of this pair of atoms. Hence if Δ is the volume of the unit cell, the energy of deformation (U) stored in the cell (s) is given by

$$\Delta U = \tfrac{1}{2} \sum_{r} \sum_{\rho\sigma} V^{\rho\sigma}_{rs} \qquad (6)$$

or

$$4\Delta U = \sum_{xr}{}' \sum_{y\rho\sigma} \{k^{y\rho\sigma}_{xrs} (q_{y\rho\sigma} - q_{yrs}) q_{xrs} + k^{x\rho\sigma}_{yrs} (q_{yrs} - q_{y\rho\sigma}) q_{x\rho\sigma}\} \qquad (6\,a)$$

the accent indicating that the term $(r, s) = (\rho, \sigma)$ is omitted in the summation of the above term.

If

$$k^{y\rho\sigma}_{xrs} = k^{x\rho\sigma}_{yrs} \qquad (7)$$

then (6) can be rewritten as

$$-4\Delta U = \sum_{xr} \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs} (q_{y\rho\sigma} - q_{yrs}) (q_{x\rho\sigma} - q_{xrs}) \qquad (8)$$

It can easily be verified that the sum of (6) for all values of the cell index s is identical with the expression (1) for the total potential energy of the crystal. The relation (7) will hold good for any atomic system under the assumptions (*a*) that the total potential energy of the system can be expressed as the sum of the mutual energies between pairs of atoms and (*b*) the mutual energy between any two atoms can be expanded as a quadratic in their relative displacements. In this case, (7) will easily follow because of the commutative property of the Taylor coefficients.

Now each lattice point of the crystal should be in equilibrium in the deformed state also and hence the resultant force acting on any atom vanishes. This leads to

$$\sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs} q_{y\rho\sigma} = 0 \qquad (9)$$

The first term in (6 *a*) now drops out in view of the relation (9). Also,

$$\sum_{xr}{}' \sum_{y\rho\sigma} k^{x\rho\sigma}_{yrs} q_{yrs} q_{x\rho\sigma} = -\sum_{xy} \sum_{r} k^{xrs}_{yrs} q_{xrs} q_{yrs}$$

Hence, the deformation energy (U) of the cell (s) is given by

$$-4\Delta U = \sum_{xr} \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\, q_{x\rho\sigma}\, q_{y\rho\sigma} \tag{10}$$

II. The strain energy function

The displacement components q_{xrs}, q_{yrs}, q_{zrs} of the atom (r, s) under a general deformation are given by

$$q_{xrs} = k_{xr} + \sum_{\bar{x}} u_{x\bar{x}}\, \bar{x}_{rs} \tag{11}$$

where x_{rs}, y_{rs}, z_{rs} are the co-ordinates of the atom (r, s) in the undeformed state and $\mathbf{k}_r = (k_{xr}, k_{yr}, k_{zr})$ $(r = 1, 2, \ldots p)$ are the inner displacements of the p interpenetrating Bravais lattices. $u_{x\bar{x}}$ .. etc., are the components of the strain which is assumed to be linear, as the applied external stresses to determine experimentally the elastic behaviour of a crystal generally lie within its elastic limits.

Substituting (11) in (10), we get

$$-4\Delta U = \sum_{xr} \sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs} \left(k_{x\rho} + \sum_{\bar{x}} u_{x\bar{x}}\, \bar{x}_{\rho\sigma}\right) \left(k_{y\rho} + \sum_{\bar{y}} u_{y\bar{y}}\, \bar{y}_{\rho\sigma}\right) \tag{12}$$

or

$$-2U = \sum_{x\rho} \sum_{y\bar{y}} \begin{Bmatrix} \rho \\ xy\bar{y} \end{Bmatrix} k_{x\rho}\, u_{y\bar{y}} + \sum_{x\bar{x}} \sum_{y\bar{y}} [x\bar{x}, y\bar{y}]\, u_{x\bar{x}}\, u_{y\bar{y}} \tag{13}$$

where

$$\begin{Bmatrix} \rho \\ xy\bar{y} \end{Bmatrix} = \frac{1}{\Delta} \sum_{r\sigma} l^{y\rho\sigma}_{xrs}\, \bar{y}_{\rho\sigma};$$

$$[x\bar{x}, y\bar{y}] = \frac{1}{2\Delta} \sum_{\rho\sigma} l^{y\rho\sigma}_{xrs}\, \bar{x}_{\rho\sigma}\, \bar{y}_{\rho\sigma}; \text{ and} \tag{14}$$

$$l^{y\rho\sigma}_{xrs} = \tfrac{1}{2}\left(k^{y\rho\sigma}_{xrs} + k^{x\rho\sigma}_{yrs}\right)$$

The term involving the product of $k_{x\rho}\, k_{y\rho}$ in (12) vanishes in view of the relations (3).

The inner displacements can be eliminated from (13) and the deformation energy can be expressed as a function of the strain components only. The equations determining them are obtained by substituting (11) in (9). They are:

$$\sum_{y\rho\sigma} k^{y\rho\sigma}_{xrs}\, k_{y\rho} = -\sum_{y\bar{y}} u_{y\bar{y}} \left(\sum_{\rho\sigma} k^{y\rho\sigma}_{xrs}\, \bar{y}_{\rho\sigma}\right) \tag{15 a}$$

or

$$\sum_{t'} (a^{\circ}_{s't'})\, k_{t'} = B_{s'} \tag{15}$$

where

$$a^{\circ}_{s't'} = \sum_{\sigma} k^{\nu\rho\sigma}_{xrs}$$

$B_{s'}$ denotes the quantity on the right-hand side of (15 *a*). By setting up a correspondence between the number-pairs $y\rho$ ($y = x, y, z$; $\rho = 1, 2, \ldots . p$) and the numbers t' ($t' = 1, 2, \ldots \; 3p$) where $t' = 3(\rho - 1) + y$ [$s' = 3(r-1) + x$] we could reduce (15 *a*) to the form (15).

The matrix $(a^0_{s't'})$ is now singular and is of rank $(3p - 3)$. We shall assume that the above equations are consistent and solvable. Then a solution of (15) is given by

$$k = \Gamma \mathrm{B} + \mathrm{B}' \tag{16 a}$$

where k is the column matrix $\{k_{t'}\}$ and B' denotes the solution of the homogeneous equations of (15). As only the relative inner displacements of the p lattices are of physical significance, we can assume without loss of generality that the inner displacement of one of the atoms (say k_n) is zero. In this case $\{\mathrm{B}'\} = \{0\}$.

Further, if we partition $(a^0_{s't'})$ in the form $\begin{pmatrix} \mathrm{C}_1 & \mathrm{C}_2 \\ \mathrm{D}_1 & \mathrm{D}_2 \end{pmatrix}$ where C_1 is a matrix containing $(3p - 3)$ rows and columns, then[7] Γ is the matrix $\begin{pmatrix} \mathrm{C}_1^{-1} & 0 \\ 0 & 0 \end{pmatrix}$. Hence, the inner displacements are given by

$$k_{xr} = - \sum_{\nu\rho} \sum_{s'\nu'} \sum_{\rho'\sigma'} u_{x'y'} \, \Gamma^{\nu\rho}_{sr} \, k^{x'\rho'\sigma'}_{\nu\rho s} \, y'_{\rho'\sigma'} \tag{16}$$

Substituting (16) in (13), we get

$$2\mathrm{U} = \sum_{x\bar{x}} \sum_{y\bar{y}} d_{x\bar{x}, y\bar{y}} \, u_{x\bar{x}} \, u_{y\bar{y}} \tag{17}$$

where

$$d_{x\bar{x}, y\bar{y}} = - [x\bar{x}, \; y\bar{y}] + (x\bar{x}, \; y\bar{y}) \tag{18}$$

and

$$(x\bar{x}, y\bar{y}) = \frac{1}{\Delta} \sum_{x'\rho} \sum_{r\sigma} \sum_{y'\rho'} \sum_{\rho_1\sigma_1} l^{\nu\rho\sigma}_{x'rs} \, \bar{y}_{\rho\sigma} \, \Gamma^{y'\rho'}_{x'\rho} \, k^{x_1\rho_1\sigma_1}_{y'\rho's} \, \bar{x}_{\rho_1\sigma_1} \tag{19}$$

Both the bracket expressions are symmetric in the pairs $x\bar{x}$, $y\bar{y}$. The symmetry $(x\bar{x}, y\bar{y})$ follows directly from the invariance conditions of the potential energy of the lattice under rigid rotations.[5]

The bracket expressions $[\bar{x}x, y\bar{y}]$ and $(\bar{x}x, y\bar{y})$ are defined in the papers of Born and Kun Huang in terms of relative displacement co-ordinates. When the relation (7) is satisfied, one can easily verify that both the forms are identical.

III. The elastic constants

If we write $e_{x\bar{x}} = (u_{x\bar{x}} + u_{\bar{x}x})$ for $\bar{x} \neq x$ and $e_{xx} = u_{xx}$, then the deformation energy obtained from the elasticity theory is a general quadratic in the six strain components e_{xx}, e_{yy}, e_{zz}, e_{yz}, e_{zx} and e_{xy}. Using Voigt's notation in which the indices (1, 2, 3, 4, 5, 6) replace respectively the symbols (xx, yy, zz, yz, zx, xy), the energy density could be written in either of these two forms.[8]

$$2U_1 = \sum_r \sum_s c_{rs} e_r e_s$$

$$= \sum_{x\bar{x}} \sum_{y\bar{y}} c_{x\bar{x}, y\bar{y}} \; e_{x\bar{x}} e_{y\bar{y}} \tag{20}$$

where the summation in the second expression is over the six different pairs given above for the indices $x\bar{x}$. The elastic constants satisfy the following symmetry relations

$$c_{x\bar{x}, y\bar{y}} = c_{x\bar{x}, \bar{y}y} = c_{\bar{x}x, y\bar{y}} = c_{y\bar{y}, x\bar{x}} \tag{21}$$

The expression (17) can be written in the form (20), if the coefficients $d_{x\bar{x}, yy}$ also satisfy the symmetry conditions (21) (*i.e.*) if

$$d_{x\bar{x}, y\bar{y}} = d_{x\bar{x}, \bar{y}y} = d_{\bar{x}x, y\bar{y}} = d_{y\bar{y}, x\bar{x}} \tag{22}$$

The coefficient $d_{x\bar{x}, y\bar{y}}$ is no doubt invariant under an interchange of the pairs ($x\bar{x}$) and ($y\bar{y}$), but its value is definitely altered under any interchange of either x and $\bar{x}$ or y and $\bar{y}$. Further, any assumption of the symmetry conditions (22) would introduce new relations among the force constants, which will lead directly to a central force-scheme, thereby spoiling the generality of the force system with which we have started. Hence, when all the nine strain components are linearly independent functions of x, y and z as in the case of heterogeneous deformations, the deformation energy is a general quadratic in all the *nine* strain components $u_{x\bar{x}}$ ($x, \bar{x} = x, y, z$) and not in the six components $e_{x\bar{x}}$. . . . only.

For a homogeneous deformation, the strain components $u_{x\bar{x}}$, etc., are independent of the space co-ordinates x, y, z of any point and are constants throughout the volume of the crystal. In this case, the strain can be analysed into a pure strain, followed by a rotation about an axis. By a suitable choice of the co-ordinate axes, it is possible to make the rotational part of the deformation vanish and the strain matrix will consequently become symmetric. The relations[1] $u_{x\bar{x}} = u_{\bar{x}x}$ ($x, \bar{x} = x, y, z$) are satisfied for all homogeneous deformations and irrotational strains. In both these cases, the expression (17) reduces to the form of the strain energy function of the

elasticity theory and one can therefore compare the coefficients of $e_{x\bar{x}}$, $e_{y\bar{y}}$ in both these expressions to obtain relations between the elastic and force constants of the crystal. The expressions for the elastic constants are therefore given by

$$c_{x\bar{x},\,y\bar{y}} = \tfrac{1}{4}\,[d_{x\bar{x},\,y\bar{y}} + d_{\bar{x}x,\,y\bar{y}} + d_{\bar{x}x,\,\bar{y}y} + d_{x\bar{x},\,\bar{y}y}] \tag{23}$$

IV. Symmetry

The displacement components q_x, q_y, q_z of a vector $\mathbf{r}=(x, y, z)$ under any small deformation are given by

$$q_x = \sum_{\bar{x}} u_{x\bar{x}}\,\bar{x} \text{ or } \mathbf{q} = \bar{\mathrm{U}}\mathbf{r} \tag{24}$$

where $\bar{\mathrm{U}}$ is the matrix $(u_{x\bar{x}})$ of the strain components and x, y, z are the components of $\mathbf{r}$ in the unstrained state.

Let the co-ordinate axes be changed to a new set of axes according to the transformation law

$$\mathbf{r}' = \mathrm{S}\mathbf{r} \tag{25}$$

Then the deformation in the new frame of reference is represented by

$$\mathbf{q}' = \bar{\mathrm{U}}'\mathbf{r}' \text{ where } \bar{\mathrm{U}}' = \mathrm{S}\bar{\mathrm{U}}\mathrm{S}^{-1} \tag{26}$$

Let S now be a symmetry operation of the crystal transforming any configuration of the crystal into another one observationally indistinguishable from it. The potential energy should be covariant under all the operations of the symmetry group of the crystal. Hence,

$$\begin{aligned} 2\mathrm{U} &= \sum_{x\bar{x}} \sum_{y\bar{y}} d_{x\bar{x},\,y\bar{y}}\, u_{x\bar{x}}\, u_{y\bar{y}} \\ &= \sum_{x\bar{x}} \sum_{y\bar{y}} d_{\,x\bar{x},\,y\bar{y}}\, u'_{x\bar{x}}\, u'_{y\bar{y}} \\ &= \sum_{x\bar{x}} \sum_{y\bar{y}} \sum_{ij} \sum_{kl} d_{x\bar{x},\,y\bar{y}}\, \mathrm{S}_{xi}\, \mathrm{S}_{yk}\, \tilde{\mathrm{S}}_{j\bar{x}}\, \tilde{\mathrm{S}}_{l\bar{y}}\, u_{ij}\, u_{kl} \end{aligned} \tag{27}$$

where we write $\tilde{\mathrm{S}} = \mathrm{S}^{-1}$.

From the above, it follows

$$2d_{ij,\,kl} = \sum_{x\bar{x}} \sum_{y\bar{y}} d_{x\bar{x},\,y\bar{y}}\,\{\mathrm{S}_{xi}\,\mathrm{S}_{yk}\,\mathrm{S}_{j\bar{x}}\,\tilde{\mathrm{S}}_{l\bar{y}} + \mathrm{S}_{xk}\,\mathrm{S}_{yi}\,\tilde{\mathrm{S}}_{l\bar{x}}\,\tilde{\mathrm{S}}_{j\bar{y}}\} \tag{28}$$

These relations reduce the number of independent constants in (17) considerably.

PART 2. THE DYNAMIC METHOD

I. The velocity of the long acoustic waves

Long waves associated with the three acoustic branches are propagated without any damping or dispersion inside the crystal. It was shown in an earlier paper[6] that the frequencies (say ω_1, ω_2, ω_3) corresponding to long waves of these three branches tend to zero and that their wave and group velocities become identical in the limit. But the expression for $\frac{d\omega}{da}$ for these three roots given there as $(-s''^{(0)}_{3p}/2s^{(0)}_{3p-1})^{\frac{1}{2}}$ is an error. We here derive a cubic equation whose roots give the values of the limiting velocities of the acoustic waves travelling in any direction of the crystal.

Differentiating the equation (10, I)

$$\sum_{t=0}^{3p} s_t z_k^{3p-t} = 0 \tag{29}$$

six times with respect to a, one obtains by Leibnitz's theorem

$$\sum_{t=0}^{3p} \sum_{s=0}^{m} \binom{m}{s} (\mathrm{D}^{m-s} s_t)\, \mathrm{D}^s (\omega_k{}^{6p-2t}) = 0 \tag{30}$$

where we write $m=6$. With the help of equation (1) of Appendix I the above equation becomes

$$\sum_{t=0}^{3p} \sum_{s=0}^{m} \sum_{r=0}^{s} \binom{m}{s} (\mathrm{D}^{m-s} s_t)\, a_{s,r}\, (6p-2t)_r\, \omega_k{}^{6p-2t-r} = 0 \tag{31}$$

where $(n)_r = n(n-1)\ldots(n-r+1)$ and $(n)_m = 0$ if $m > n$.

Now s_{3p}, s_{3p-1}, s_{3p-2} are equal to the sums of products of the roots of (29) taken respectively $3p$, $(3p-1)$, $(3p-2)$ times and therefore are zero for $a=0$. By direct differentiation of these expressions, it can be verified that the first non-vanishing derivatives of these three coefficients for $a=0$ are $s^{(6)}_{3p}{}^{(0)}$, $s^{(4)}_{3p-1}{}^{(0)}$ and $s''_{3p-2}{}^{(0)}$ respectively, as the derivatives of lesser orders of s_{3p}, s_{3p-1}, and s_{3p-2} are expressible as sums of terms, each containing at least one factor ω_k $(k=1, 2, 3)$ or products and squares of them. Again, as the terms in the left-hand side of (31) are continuous functions of the variable a, the limit for $a=0$ could be obtained by writing $\omega_k=0$; $s^{(i)}_{3p}{}^{(0)}=0$ $(i=0, 1, 2\ldots.5)$; $s^{(i)}_{3p-1}{}^{(0)}=0$ $(i=0, 1, 2, 3)$ and $s^{(i)}_{3p-2}{}^{(0)}=0$ for $i=0, 1$. In proceeding to the limit, we note that all terms excepting those for which $r=s=(6p-2t)$ $(3p-t=0, 1, 2, 3)$ on the L.H.S. of (31) contain either powers of ω_k or $(n)_m$ with $m>n$ or derivatives of s_{3p},

s_{3p-1} and s_{3p-2} with respect to a of order less than 6, 4 and 2 respectively. Equating the sum of these four terms to zero, we obtain

$$720\, a_0 y^3 + 360\, a_1 y^2 + 30\, a_2 y + a_3 = 0 \tag{32}$$

where

$$a_0 = s^{(0)}_{3p-3};\quad a_1 = s''^{(0)}_{3p-2};\quad a_2 = s^{(4)}_{3p-1\ (0)};\quad a_3 = s^{(6)}_{3p\ (0)};\ \text{and}$$

$$y = \left(\frac{d\omega}{da}\right)^2.$$

If $\mathbf{a} = \mathbf{e}a$, then y denotes the square of the limiting group velocity of the acoustic waves in the direction of the vector $\mathbf{e}$. a_0 is independent of $\mathbf{e}$ and is the same for all directions, but a_1, a_2 and a_3 are clearly functions of the vector $\mathbf{e}$. The roots of (32) therefore give the three possible velocities of sound waves of thermal origin travelling in the direction $\mathbf{e}$ of the crystal.

For the actual numerical evaluation of the coefficients of the various powers of y in (32), we observe that the elements of the matrix[6] $\mathrm{A} = (a_{s't})$ can be expanded as a power series in a as they involve only sine and cosine terms. Hence a_1, a_2, a_3 are equal to the coefficients of $\frac{a^2}{2!}$, $\frac{a^4}{4!}$ and $\frac{a^6}{6!}$ in the Maclaurin expansion of s_{3p-2}, s_{3p-1} and s_{3p} respectively.

II. Wave propagation in crystals

The equations determining the velocities and direction of vibration of the elastic waves in terms of their direction of propagation can be obtained from the variational equations derived from Hamilton's principle. The total kinetic energy of the body is given by

$$2\mathrm{T} = \int \rho\, (\dot{u}_x^2 + \dot{u}_y^2 + \dot{u}_z^2)\, d\mathrm{V} \tag{33}$$

and the work done by the external forces for a small displacement is expressed by

$$\delta \mathrm{W}_1 = \sum_z \int \rho\, (\mathrm{T}_x\, \delta u_x)\, d\mathrm{V} + \sum_z \int (\mathrm{T}_{xv}\, \delta u_x)\, d\mathrm{S} \tag{34}$$

Here T_x, T_y, T_z are the body forces per unit volume acting on the element $d\mathrm{V}$ and $\mathrm{T}_{\bar{x}v} = (\mathrm{T}_{\bar{x}x}, \mathrm{T}_{\bar{x}y}, \mathrm{T}_{\bar{x}z})$ $(\bar{x} = x, y, z)$ are the surface tractions acting on the surface element $d\mathrm{S}$. We shall assume that all the nine strain components $u_{x\bar{x}} = \frac{\partial u_x}{\partial \bar{x}}$ $(x, \bar{x} = x, y, z)$ are linearly independent functions of the space co-ordinates x, y, z and further take the relation (7) to be true. The potential energy of deformation is given by (17) so that we have,

$$\delta \int_{t_0}^{t_1} \mathrm{V}\, dt = \delta \int_{t_0}^{t_1} dt \int \mathrm{U}\, d\mathrm{V}$$

$$= \int_{t_0}^{t_1} \left\{ \int \sum_{x\bar{x}} \left(\frac{\partial \mathrm{U}}{\partial u_{x\bar{x}}} \delta u_{x\bar{x}} \right) d\mathrm{V} \right\} dt \tag{35}$$

We have now from Hamilton's principle

$$\delta \int (\mathrm{T} - \mathrm{V})\, dt + \int \delta \mathrm{W}_1 dt = 0 \tag{36}$$

The Euler variational equations can be set up in the usual way and these are expressed by

$$\rho \frac{\partial^2 u_x}{\partial t^2} = \rho \mathrm{T}_x + \frac{\partial \mathrm{T}_{xx}}{\partial x} + \frac{\partial \mathrm{T}_{xy}}{\partial y} + \frac{\partial \mathrm{T}_{xz}}{\partial z} \tag{37}$$

$$= \rho \mathrm{T}_x + \sum_{\bar{x}} \frac{\partial}{\partial \bar{x}} \left(\frac{\partial \mathrm{U}}{\partial u_{x\bar{x}}} \right) \qquad (x = x,\ y,\ z)$$

together with the equations

$$\mathrm{T}_{x\nu} = \sum_{y} \frac{\partial \mathrm{U}}{\partial u_{xy}} \cos(y,\ \nu) \tag{38}$$

determining the state of motion at the surface of the body. A set of functions $(u_x,\ u_y,\ u_z)$ satisfying the equations (37) and (38) represent the possible components of vibration of the elements of the elastic body.

If we assume plane wave solutions for the above equations of the form

$$u_x = \mathrm{A}^x e^{i(wt - a.r)} \tag{39}$$

then substitution of (39) in (37) leads to [for the case $(\mathrm{T}_x = \mathrm{T}_y = \mathrm{T}_z = 0)$]

$$\rho v^2 \mathrm{A}^x = \sum_{\bar{x}} \sum_{y\bar{y}} d_{x\bar{x},\, y\bar{y}}\, \mathrm{e}_{\bar{x}}\, \mathrm{e}_{\bar{y}}\, \mathrm{A}^y \tag{40}$$

Writing $\mathrm{A} = (\mathrm{A}^x,\ \mathrm{A}^y,\ \mathrm{A}^z)$ and $\mathrm{D}_{xy} = \sum_{\bar{x}_y} d_{x\bar{x},\, y\bar{y}}\, \mathrm{e}_{\bar{x}} \mathrm{e}_{\bar{y}}$, we can rewrite the above equations as $(\mathrm{D} - \rho v^2)\, \mathrm{A} = 0$. The matrix $\mathrm{D} = (\mathrm{D}_{xy})$ is symmetric and hence its eigenvalues are real. If they are distinct, the corresponding eigenvectors are mutually orthogonal. Hence the vibration directions of the three wavefronts moving in any direction are mutually perpendicular to each other, but they may be obliquely inclined to their direction of propagation.

Equations (40) are the Begbie-Born equations for the long acoustic waves of the crystal. Born and Begbie held the relations (22) to be true, even for a general force system and derived the expressions $c_{x\bar{x},\, y\bar{y}} = d_{x\bar{x},\, y\bar{y}}$

for the elastic constants. Clearly, their contention is untenable, as the Cauchy relations can be shown to be a direct consequence of the relations (22) for crystals with a centre of symmetry. For such crystals, the round brackets in (18) vanish[5] and so $d_{x\bar{x},\, y\bar{y}} = -[x\bar{x}, y\bar{y}]$. In view of the interchangeability of x and y or $\bar{x}$ and $\bar{y}$ in the square brackets, we have now from (22)

$$d_{xx,\, yy} = d_{yx,\, xy} = d_{xy,\, xy}, \cdots$$

and

$$d_{xx,\, yz} = d_{xz,\, yx} = d_{zx,\, xy}$$

The Cauchy relations are now a matter for mere verification. Hence the expressions of Begbie and Born for the elastic constants are not valid for a general force-scheme and are true for central force systems only. A second attempt to derive expressions for the elastic constants by a comparison of (40) with the elastic wave equations was made of Kun Huang, but he could do so only after the explicit introduction of certain additional conditions like $[x\bar{x}, y\bar{y}] = [\bar{x}x, \bar{y}y]$, etc., which he interpreted as the conditions for the vanishing of the initial stresses in an infinite lattice. That such additional conditions had to be imposed is not surprising, for equations (40) involve 45 independent constants whereas the equations of the elasticity theory contain only 21 constants. Further, the equations (40) are derived from a potential function containing the rotational components of the strain also, while the equations of the elasticity theory are derived from a potential involving the six strain components only and hence these two cannot generally be reduced to the same form. As mentioned earlier, any assumption of new relations—other than those supplied by the invariance conditions of the potential energy under translations and rigid rotations—has no theoretical justification. So, the expressions given by Kun Huang for the elastic constants are also not reliable and correct.

The equations (40) fail to hold good for the case $u_{x\bar{x}} = u_{\bar{x}x}$ $(x, \bar{x} = x, y, z)$. In this case, the deformation energy is a function of the six strain components only and the equations obtained by the variational method are identical with the equations of the elasticity theory. The latter can always be used to find the velocities of any disturbance generated inside the crystal, provided the stresses produced by the wave-fronts are uniform throughout its volume and their wavelengths are large compared to the dimensions of the unit cell. As longitudinal waves are strictly irrotational, their velocities can be deduced from the elastic wave equations only. The vibration directions and velocities of quasi-torsional waves, on the other hand, are determined by the equations (40).

III. The elastic constants of diamond

The elastic constants and vibration spectrum of diamond has recently been a subject of numerous investigations by various authors.[9, 10, 11] We here briefly sketch the application of the preceding sections to the evaluation of the elastic constants of diamond. For the notation used and other details, the reader is referred to the papers of Krishnamurti and Ramanathan.[9, 10]

The symmetry operations which we use to reduce (17) to its simplest form are:

(*a*) S_1: a rotation by $\frac{2\pi}{3}$ about the line $x=y=z$.

(*b*) S_2: a reflection in the plane $x=y$.

(*c*) S_3: a rotation by $\frac{\pi}{2}$ about a line parallel to the z-axis through the point $\left(\frac{d}{4}, \frac{d}{4}, \frac{d}{4}\right)$ followed by another rotation through $\frac{\pi}{2}$ about an axis through the same point parallel to the x-axis.

The matrix $\bar{U}=(u_{x\bar{x}})$ transforms under these three operations into

$$(a)\ \bar{U}_1' = S_1 \bar{U} S_1^{-1} = \begin{pmatrix} u_{yy} & u_{yz} & u_{yx} \\ u_{zy} & u_{zz} & u_{zx} \\ u_{xy} & u_{xz} & u_{xx} \end{pmatrix}$$

$$(b)\ \bar{U}_2' = S_2 \bar{U} S_2^{-1} = \begin{pmatrix} u_{yy} & u_{yx} & u_{yz} \\ u_{xy} & u_{xx} & u_{xz} \\ u_{zy} & u_{zx} & u_{zz} \end{pmatrix} \tag{41}$$

$$(c)\ \bar{U}_3' = S_3 \bar{U} S_3^{-1} = \begin{pmatrix} u_{yy} & u_{yz} & -u_{yx} \\ u_{zy} & u_{zz} & -u_{zx} \\ -u_{xy} & -u_{xz} & u_{xx} \end{pmatrix}$$

We have used in the above the matrix forms for S_1, S_2 and S_3 given in Smith's paper.[11]

By setting up a correspondence between the symbols (xx, yy, zz, yz, zy, zx, xz, xy, yx) and the numbers (1, 2, 3, 4, 5, ... 9), we can conveniently write the constants $d_{x\bar{x}, y\bar{y}}$ in the form d_{ij} with two indices only.

From (41) we obtain with the help of (27) the following relations:

$$d_{11}=d_{22}=d_{33};\quad d_{12}=d_{23}=d_{31};\quad d_{45}=d_{67}=d_{89}.$$

$d_{44}=d_{55}=d_{66}=d_{77}=d_{88}=d_{99}$. All other constants in (17) are zero. Thus for cubic crystals of the O_h class, the number of independent constants in (17) is four.

The values of the above constants expressed in terms of the force constants are given by

$$\begin{aligned}
d_{11}=d_{xx,\,xx}&=-\frac{(Q+8U+2\alpha+9\delta)}{d}\\
d_{12}=d_{xx,\,yy}&=-\frac{(R+4W-6\beta+\gamma)}{d}\\
d_{45}=d_{yz,\,zy}&=-\frac{(R+4W-6\beta+\gamma)}{d}+\frac{(R+2\beta-3\gamma)^2}{(Q+3\Sigma)}\times\frac{1}{d}.\\
d_{44}=d_{yz,\,yz}&=-\frac{1}{d}(Q+4S+4U+10\alpha+\delta)+\frac{1}{d}\frac{(R+2\beta-3\gamma)^2}{(Q+3\Sigma)}
\end{aligned}\tag{42}$$

Hence from (23) the expressions for the elastic constants are:

$$\begin{aligned}
c_{11}&=d_{11};\\
c_{12}&=d_{12};\\
c_{44}&=\tfrac{1}{2}(d_{44}+d_{45});\\
&=-\frac{1}{2d}\{Q+R+4(S+U+W)+10\alpha+\delta+\gamma-6\beta\}\\
&\qquad+\frac{(R+2\beta-3\gamma)^2}{d(Q+3\Sigma)}
\end{aligned}\tag{43}$$

which are identical with the expressions of Krishnamurti.

To arrive at an estimate of the discrepancies in the values of the elastic constants calculated by the two different procedures, we shall next express the elastic-force constant relations by comparing the lattice wave-equations (40) with the elastic wave equations. The former are given by

$$\rho v^2 A^x = A^x\{d_{11}l^2+d_{44}(m^2+n^2)\}+(d_{12}+d_{45})(A^y lm+A^z ln) \tag{44}$$

and two similar equations obtained by cyclic permutation of the letters x, y, z and l, m, n. Comparing (44) with the equation

$$\rho v^2 A^x = A^x\{c_{11}l^2+c_{44}(m^2+n^2)\}+(c_{12}+c_{44})(A^y lm+A^z ln) \tag{45}$$

we obtain*

$$c_{11} = d_{11};$$

$$c_{44} = d_{44}; \text{ and}$$

$$c_{12} = d_{12} + d_{45} - d_{44} \qquad (46)$$

$$= \frac{(Q + 4S + 4U + 10\alpha + \delta)}{d} - \frac{2(R + 4W - 6\beta + \gamma)}{d}$$

These expressions are different from those of (43). The expression for c_{11} is the same in both the cases. The numerical values of the force constants were obtained by Ramanathan from spectroscopic data. If these values are substituted in (43) and (46), we get the following numerical values for the elastic constants of diamond, calculated by the two different procedures.

$$c_{11} = 9{\cdot}6 \times 10^{12}\ (9{\cdot}6 \times 10^{12});\quad c_{12} = 3{\cdot}9 \times 10^{12}\ (1{\cdot}49 \times 10^{12});$$

$$c_{44} = 4{\cdot}2 \times 10^{12}\ (5{\cdot}39 \times 10^{12})\ \text{dynes/cm.}^2$$

The elastic constants of diamond were determined experimentally by Bhagavantam and Bhimasenachar who get the following values:

$$c_{11} = 9{\cdot}5 \times 10^{12};\quad c_{12} = 3{\cdot}9 \times 10^{12};\quad c_{44} = 4{\cdot}3 \times 10^{12}\ \text{dynes/cm.}^2$$

While the expressions of Krishnamurti show a very good fit with the experimental data of Bhagavantam and Bhimasenachar, the values calculated from (46) show significant divergences from these results.

Finally, the author wishes to express his deep gratitude to Professor Sir C. V. Raman, F.R.S., N.L., for his inspiring guidance and valuable criticisms during the course of this work.

SUMMARY

The static method of obtaining the strain energy function of a crystal has been developed for the case where the potential energy of the entire lattice is a general quadratic in the nuclear displacements of the atoms of the crystal. It is shown that for heterogeneous strains, the deformation energy of the crystal is a quadratic in all the nine strain components. For small homogeneous deformations, the strain energy function reduces to the form of the corresponding function in the elasticity theory. The wave equations obtained from this energy function by the variational procedure are

* These expressions for diamond based on the dynamic method were obtained by Mr. D. Krishnamurti and independently by Dr. J. Callaway, R. C. A. Laboratories, Princeton, N.J. I am indebted to Mr. D. Krishnamurti for pointing out the discrepancies in the expressions arising out of these two theoretical procedures and for the general discussions on the subject.

identical with the wave equations of the elasticity theory. By comparing either the two forms of the strain energy function or the two sets of wave-equations, expressions for the elastic constants can be obtained in terms of the atomic force constants.

Starting from the most general expression for the strain energy function which is a quadratic in all the nine strain components and by assuming that the strain components are all linearly independent functions of the position vector of any point of the solid, the wave equations of Begbie and Born have been derived by means of Hamilton's variational principle. But these equations are not reducible to the symmetric form of the wave equations of the elasticity theory without further assumption of additional relations among the force constants. Since there is no justification for such new relations which restrict the generality of the force scheme used, the expressions of Begbie-Born and of Kun Huang for the elastic constants of crystals are not valid in a general force scheme. The expressions for the elastic constants which follow the different theoretical procedures are derived for the case of diamond and are compared with the experimental results.

Finally, a cubic equation whose roots determine the limiting group velocities of the long acoustic waves travelling in any direction of the crystal, has been derived; this replaces the expression for the velocities of the long acoustic waves given in an earlier paper by the author.

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APPENDIX I

Lemma.—If ω is a continuous function of the variable a with continuous derivatives with respect to a of order upto N in (α, β) and D denotes the operator $\left(\frac{d}{da}\right)$, then $D^n = \sum_{r=0}^{n} a_{n,r} \left(\frac{d}{d\omega}\right)^r$ in (α, β) $(n \leqslant N)$ (1)

where

$$a_{n,r} = \Sigma \frac{n!\,(D^{r_1}\omega)^{a_1}(D^{r_2}\omega)^{a_2}\ldots(D^{r_s}\omega)^{a_s}}{(r_1!)^{a_1}a_1!\,(r_2!)^{a_2}a_2!\ldots(r_s!)^{a_s}a_s!} \text{ for } (r>0); \quad (2)$$

$a_{n,0} = \delta_{n0}$;

$n = a_1r_1 + a_2r_2 + \ldots + a_sr_s$ and

$r = a_1 + a_2 + \ldots + a_s$; the summation in (2) is over all the partitions of n into r non-zero integral parts.

Proof.—$D_1, D_2, \ldots D_r$ being r mutually commuting operators, we first define the symbol $(D_1^{p_1}D_2^{p_2}\ldots D_r^{p_r})\,\omega$ as equivalent to the scalar expression $(D_1^{p_1}\omega)\,(D_2^{p_2}\omega)\ldots(D_r^{p_r}\omega)$. With this convention, consider the multinomial expansion $\frac{1}{r!}(D_1+D_2+\ldots+D_r)^n\omega = \frac{1}{r!}\Sigma\frac{n!}{n_1!\,n_2!\ldots n_r!}$ $(D_1^{n_1}\omega)\ldots(D_r^{n_r}\omega)$ where $\sum_{s=1}^{r} n_s = n$. $a_{n,r}$ can now easily seen to be the expression obtained by writing $D_1 = D_2 = \ldots\ldots = D_r = D$ in the sum of all the terms of the above expansion which arise from a partition of n into r non-zero integral parts. We have now for $n=1$ and $n=2$,

$$D = \frac{d\omega}{da} \times \frac{d}{d\omega} \quad \text{and}$$

$$D^2 = (D^2\omega)\frac{d}{d\omega} + (D\omega)^2\frac{d^2}{d\omega^2}$$

Evidently D^n is of order n in $\left(\frac{d}{d\omega}\right)$ and hence can be expressed by a series of the form (1). Again, by differentiating (1) with respect to a and comparing the result with

$$D^{n+1} = \sum_{r=1}^{n+1} a_{n+1,r}\left(\frac{d}{d\omega}\right)^r,$$

we obtain

$$a_{m+1,r} = a_{m,r-1}\left(\frac{d\omega}{da}\right) + \frac{da_{m,r}}{da} \quad (3)$$

If therefore (3) can be proved on the assumption that (2) is valid for all values of n upto m, then the lemma will easily follow by induction as it is true for $n=1$ and $n=2$.

By definition $a_{m+1,r}$ is the sum of all the terms involving the products of *all* the r operators in the expression

$$(D_1+D_2+\ldots+D_r)\frac{1}{r!}(D_1+D_2+\ldots+D_r)^m \qquad (4)$$

if in the final result D is substituted in the place of all the D_i's. Such terms arise in two ways. (*a*) They could for example be obtained by multiplying D_i with the terms containing $(r-1)$ factors in the expansion of $\frac{1}{r!}(D_1+D_2+\ldots+D_{i-1}+D_{i+1}+\ldots D_r)^m\omega$ and as i takes r values, the sum of all such terms reduces to $a_{m,r-1}\frac{d\omega}{da}$ when in the final result we write $D_i=D$. (*b*) They can arise by multiplying the first (linear) term in (4) with the terms involving the products of all the D_i's in the expansion of $\left(\sum_{i=1}^{r} D_i\right)^m\omega$. Taking a typical term $k\,(D_1^{p_1}D_2^{p_2}\ldots D_r^{p_r})\omega$ where $k=\frac{m!}{\Pi p_r!}$ arising out of this partition of m into r factors, the result of multiplying this term with $\left(\sum_{i=1}^{r} D_i\right)$ is evidently

$$k\sum_{i=1}^{r}(D_1^{p_1}\omega)\ldots(D_i^{p_i+1}\omega)\ldots(D_r^{p_r}\omega) \qquad (5)$$

As the expression obtained by writing $D_i=D\,(i=1,2,\ldots r)$ in (5) is the differential coefficient of $k\,(D^{p_1}\omega)\ldots(D^{p_r}\omega)$, the sum of all the terms under consideration is clearly $\frac{da_{n,r}}{da}$. This establishes the result (3) and consequently the lemma by induction.

In particular, we note that $a_{n,n}=\left(\frac{d\omega}{da}\right)^n$.

ERRATA

THE PREPARATION OF LARGE NUCLEAR EMULSION DETECTORS AND THEIR APPLICATION TO THE STUDY OF K-MESONS AND HYPERONS

(*Proc. Ind. Acad. Sci.*, *XXXVIII*, 277, 1953)

D. LAL, YASH PAL AND B. PETERS
(Tata Institute of Fundamental Research, Bombay)

IN the bibliography of the above-named paper we inadvertently omitted an article by Pierre Demers (*Can. J. Res.*, **28 A**, 628, 1950). Demers at that time not only realized the usefulness of constructing a particle detector with superimposed unbacked emulsion sheets, but also constructed such detectors and applied them to the study of nuclear disintegrations. We regret the oversight and are grateful to Dr. Demers for drawing our attention to his earlier research work. While the method described in our paper is, therefore, not new, an appreciable increase in accuracy of alignment was achieved which has greatly extended the range of applicability of this technique.

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ERRATA

Vol. XXXIX, No. 3, *Sec. A, March* 1954

Under References Page 131 :

1. *Substitute* in 2nd col. of item 3 "*Ibid.*, 1952, **43**, 753" *in place* of "*Ibid.*, 1953, **63**, 753".
2. *Add* in the 1st col. of item 7 the name "Swamy, M. S." *after* the name of "Peters, B."

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